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THE THEORY AND APPLICATION OF COLLOIDAL BEHAVIOR

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THE THEORY AND APPLICATION OF COLLOIDAL BEHAVIOR

Contributed by the foremost authorities in each division of the subject

ROBERT HERMAN BOGUE, PH.D. (EDITOR)
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VOLUME I

THE THEORY OF COLLOIDAL BEHAVIOR

FIRST EDITION
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PREFACE

As recently as ten to fifteen years ago, "colloid chemistry" received none but the most casual reference, either in the literature, or in the text-books on physical chemistry. It was not recognized, at that time, as a subject deserving of any especial or involved consideration. And yet it had been fifty years since Thomas Graham pointed out the essential characteristics of the colloid state.

In those fifty years, investigators had not altogether neglected this condition of matter. But, in their studies of it, they had not understood the fundamental laws governing the behavior of the colloid state, and so failed entirely to build up a rational theory. Their work pointed only to empirical effects which were not explained by the laws of classical chemistry. The real contributions during this period were, therefore, confined to certain physical effects of particle size. Since no general theory was evolved, any intelligent application based upon colloidal behavior was impossible. This explains the general neglect of the subject, during that period, by the average physical and industrial chemist.

The first physico-chemical theory that could be applied directly to the explanation of colloidal behavior was suggested by Professor F. G. Donnan of the University of London in 1911, and three years later Professor Henry Procter of the University of Leeds made use of the theory to explain the swelling of gelatin. This was the first attempt to account stoichiometrically, and by a principle of physical chemistry which was based upon the undisputed laws of thermodynamics, for a property that is recognized as distinctly and uniquely colloidal. The outstanding work of the late Doctor Jacques Loeb, during the past six years, has carried over the explanation, also upon strictly stoichiometric grounds, and upon the principle laid down by Donnan, to other properties which may be regarded as characteristic of the colloid state, at least insofar as the behavior of

the proteins is concerned. That this principle is not confined to the protein colloids, but applies also, and with equal completeness and surety, to the lyophobic colloids, has been postulated by John Arthur Wilson, and experimental verification has been produced by Professor H. T. Beans and his students at Columbia University, working particularly with gold sols. The relation of particle size to the general theory has been pointed out by the editor of this work. This brings us to the present moment in our attempt to explain colloidal behavior on a rational basis. There must follow much intensive work to establish the validity of a general theory and the field must be broadened to include the non-aqueous systems. This should be accomplished in the next few years.

Meanwhile the industrial chemist, the agricultural chemist, and the physiological chemist had not been idle but, sensing the importance of the new science, for it was now growing so rapidly that it could be regarded as such, they had, in a multitude of cases, applied these principles to their individual problems, and were meeting with astonishing and successful results. As these multiplied, the demand for more information, both of a theoretical and of a practical nature, became apparent. A few books appeared bearing on special phases of the matter, as those by Bancroft, Loeb, Wilson, and the present editor. But a comprehensive treatise was demanded, and this book is an attempt to meet that need.

In a subject of such universal application, it is quite impossible for one man to become so well informed on each aspect as to justify his attempt to write such a book by his own hand alone. The cooperative treatise presents certain inherent difficulties, such as an overlapping of material presented, occasional differences in point of view, and differences of opinion as to relevant subject matter. While these cannot be entirely avoided, and it is not always desirable that they should be avoided, the advantages of such a cooperative undertaking are overwhelmingly obvious.

While attention has been given to covering every important theoretical aspect, and many of the most conspicuous of the direct applications that have been made in industry, agriculture, geology, medicine, etc., yet, in the treatment of the applied field, a great many subjects that are unquestionably concerned with

colloid phenomena are not given space in this treatise. There are three reasons for this. First, to cover every possible application would necessitate a series of many volumes, and as the size and expense increase, the usefulness to the average chemist or investigator diminishes. Second, the science is still so young that chemists thoroughly familiar with the modern colloid point of view are to be found but rarely in industry. Third, a few typical instances, such as are contained in the chapters of Volume II, will serve very well to draw to the attention of chemists the remarkable rôle that colloidal behavior plays in nearly every phase of living or inanimate processes. The editor makes no apology for not including the many hypotheses and experimental findings that have been published from time to time, but which have been found to be in error, and, therefore, to contribute nothing of value to the modern concept.

This plan has evolved a work that has a direct and purposeful objective, and it will prove the more useful to the greater number of students of colloidal behavior. Every large college and university is now offering some work, at least to graduate students, in colloid chemistry. Many books are available for an elementary presentation. But no attempt has heretofore been made to gather together material for an advanced text or reference work, nor to present the actual application of the science. The editor believes that these ends are achieved by the publication of this book. It is written for the student and the investigator, the research man and the practical man, who, in science or in industry, is concerned with the problems of colloidal behavior.

It is a pleasure to acknowledge the hearty cooperation of the contributors who have made this work possible. Whatever of value may lie in the book, the credit belongs to the men who have given generously of their time and energy in the furtherance of a cause to which they are devoting their lives.

The editor feels deeply the untimely death of our friend and associate, Doctor Jacques Loeb. The masterful chapter which he contributed for this book constitutes the finest exposition of his matured concept of colloidal behavior that has come from his pen. It was his last writing on the subject, and the most clearly and concisely expressed. New workers must carry on where he left off.

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COLLOIDAL BEHAVIOR

CHAPTER I

APPLICATION OF THE THERMODYNAMICS OF HETEROGENEOUS EQUILIBRIA TO THE THEORY OF COLLOIDAL PHENOMENA

By

John Arthur Wilson

Much of the complexity of colloidal phenomena may be ascribed to the polyphase nature of the systems with which they are associated, the difficulty of recognizing and locating the boundaries of all of the phases present, and to the presence of ions, or electrically charged masses, the free diffusion of which between the several phases is prevented by one cause or another. Although the reactions occurring within the boundaries of any single phase may be relatively very simple, yet the behavior of the polyphase system, as a whole, may appear bewilderingly complex if the existence of any one phase is overlooked. In this chapter we shall present the viewpoint of a growing school of thought that looks upon colloidal phenomena as a manifestation of certain types of heterogeneous equilibria determinable quantitatively by means of thermodynamics and well-established laws of physical chemistry. Membrane, jelly, and surface equilibria will be discussed in turn.

Membrane Equilibria

In 1911, Donnan[1] propounded a theory, based upon the well-known distribution law, to account for the type of equilibrium resulting from the separation by a membrane of two solutions, one of which contains an ionogen having one ion that cannot

[1] Donnan, F. G.: *Z. Elektrochem.*, **17** (1911), 572.

diffuse through the membrane, which is permeable to all other ions of the system. As an example, Donnan takes an aqueous solution of a salt NaR, such as Congo red, in contact with a membrane which is impermeable to the anion R′ and the non-ionized salt NaR, but will allow water and Na^+, or any other ion, to pass freely through it. The membrane separates the Congo red solution from an aqueous solution of sodium chloride, which will diffuse from its Solution II into the Solution I of NaR.

The first problem is to determine how the sodium chloride will distribute itself between the solutions on the two sides of the membrane. When equilibrium is established, if a small virtual change is made reversibly at constant temperature and volume, the free energy will remain unchanged; that is, no work will be done. The change here considered is the transfer of *dn* mols of Na^+ and Cl' from II to I. The work, which equals zero, is

$$dn.\mathrm{RT}.\log_e \frac{[Na^+]_{II}}{[Na^+]_I} + dn.\mathrm{RT}.\log_e \frac{[Cl']_{II}}{[Cl']_I} = 0$$

whence $$[Na^+]_{II} \times [Cl']_{II} = [Na^+]_I \times [Cl']_I$$

(The brackets indicate concentration in mols per liter.) Equilibrium will be established only when the product of the concentrations of Na^+ and Cl' has the same value on both sides of the membrane.

Since this equation of products is of vital importance to the quantitative development of the theory here presented, any doubt as to its validity should be dispelled at the outset. The derivation of the equation need not involve the use of thermodynamics, because it can readily be visualized. In passing from one phase to the other, the oppositely charged ions must move in pairs, since they would otherwise set up powerful electrostatic forces that would prevent their free diffusion. For this reason, a sodium or a chlorine ion striking the membrane alone could not pass through it. But, since the membrane is freely permeable to both Na^+ and Cl', when two oppositely charged ions strike the membrane together, there is nothing to prevent them from passing through into the solution on the opposite side. The rate of transfer of these ions from one solution to the other depends, therefore, upon the frequency with which they chance to strike the membrane in pairs, which is measured by the product of their

concentrations. At equilibrium, the rate of transfer of Na^+ and Cl' from Solution II to Solution I exactly equals the rate of transfer of these ions from Solution I to Solution II, from which it follows that the product of the concentrations of these ions has the same value in both solutions.

We may now consider the effect of adding another salt, such as KBr, to the system. Following the same line of reasoning, it will be evident that equilibrium will be established only when the product $[K^+] \times [Br']$ has the same value on both sides of the membrane and the same will be true for the products $[K^+] \times [Cl']$ and $[Na^+] \times [Br']$. In fact, with any number of monomonovalent ionogens present in the system, the product of the concentrations of any pair of diffusible and oppositely charged ions will have the same value in both solutions.

Introducing polyvalent ions into the system makes the equation of products but very little more complicated. When a polyvalent ion strikes the membrane, it will pass through only when an equivalent number of ions of opposite sign strike the membrane at the same time and pass through with it. The rate of transfer of any dissociated ionogen from one solution to the other is evidently determined by the product of the concentrations of all of the ions required to produce the undissociated ionogen. At equilibrium, this product will have the same value in both solutions. If, for example, the system contained the ions Na^+ and SO_4'', then the product $[Na^+] \times [Na^+] \times [SO_4'']$, or $[Na^+]^2 \times [SO_4'']$, would have the same value on both sides of the membrane, at equilibrium.

With the equation of products as a starting point, we may now consider further the nature of the unequal distribution of ions between the two solutions, caused by the impermeability of the membrane to the anion R′. In Solution II of the simple system including only the ionogens NaR and NaCl, let

$$x = [Na^+] = [Cl']$$

In Solution I let $y = [Cl']$

and $z = [R']$

whereupon $[Na^+] = y + z$

The equation of products may then be written

$$x^2 = y(y + z)$$

But here we have the product of equals equated to the product of unequals, from which it is apparent, mathematically, that the sum of the unequals is greater than the sum of the equals, or that

$$2y + z > 2x$$

The reasoning thus indicates that the concentration of diffusible ions in Solution I, at equilibrium, is greater than in Solution II. If we let the excess of concentration of diffusible ions of Solution I over Solution II be represented by e, then

$$2y + z = 2x + e$$

and

$$x = y + \sqrt{ey}$$

which shows us further that x is greater than y, or that the concentration of ionized sodium chloride is greater in Solution II than in Solution I. The added sodium chloride does not distribute itself equally throughout both solutions, but is the more concentrated in Solution II, at equilibrium.

The different distribution of ions in the solutions at equilibrium gives rise, not only to a difference in osmotic pressure, but also to an electrical difference of potential across the membrane. Donnan derived the equation for this potential difference by the following thermodynamic reasoning.

In the system just described, let π_{I} be the potential, for positive electricity, of Solution I, and π_{II} that for Solution II. Let the extremely small quantity Fdn of positive electricity be transferred isothermally from II to I. In this virtual change of the system from equilibrium, the following work terms must be considered: The change in free electrical energy represented by $Fdn(\pi_{\text{I}} - \pi_{\text{II}})$ and the simultaneous transfer of pdn mols of Na^+ from II to I and of qdn mols of Cl' from I to II, where p and q are the respective transport numbers of the ions, and, hence, $p + q = 1$. The maximum osmotic work of operation of this transfer of ions is represented by the expression

$$pdn.\text{RT}.\log_e \frac{[Na^+]_{\text{II}}}{[Na^+]_{\text{I}}} + qdn.\text{RT}.\log_e \frac{[Cl']_{\text{I}}}{[Cl']_{\text{II}}}$$

But, since the system is in equilibrium, the electrical virtual work must balance the osmotic virtual work, or

$$Fdn(\pi_{\text{I}} - \pi_{\text{II}}) = pdn.\text{RT}.\log_e \frac{[\text{Na}^+]_{\text{II}}}{[\text{Na}^+]_{\text{I}}} + qdn.\text{RT}.\log_e \frac{[\text{Cl}']_{\text{I}}}{[\text{Cl}']_{\text{II}}}$$

But $\frac{[\text{Na}^+]_{\text{II}}}{[\text{Na}^+]_{\text{I}}} = \frac{[\text{Cl}']_{\text{I}}}{[\text{Cl}']_{\text{II}}} = \frac{x}{y}$ and $p + q = 1$. Letting $E = \pi_{\text{I}} - \pi_{\text{II}}$, we have

$$E = \frac{\text{RT}}{F} \log_e \frac{x}{y} \text{ volts}$$

This is an equation of fundamental importance in dealing quantitatively with the electrical phenomena associated with colloidal behavior.

It will now be shown that this equation is still valid when other ions of any valency are added to the system. Consider the general case where an ionogen yielding the ion M^{a+} of valency a is added. By applying the above line of reasoning to the potential difference produced by the unequal distribution of the ions of the added ionogen between Solution I and Solution II, we arrive at the equation

$$E = \frac{\text{RT}}{nF} \cdot \log_e \frac{[\text{M}^{a+}]_{\text{II}}}{[\text{M}^{a+}]_{\text{I}}}$$

where $n = a$, the valency of M^{a+}. But it is evident from the equation of products that

$$[\text{M}^{a+}]_{\text{I}} \times [\text{Cl}']^a_{\text{I}} = [\text{M}^{a+}]_{\text{II}} \times [\text{Cl}']^a_{\text{II}}$$

and that

$$[\text{Na}^+]^a_{\text{I}} \times [\text{Cl}']^a_{\text{I}} = [\text{Na}^+]^a_{\text{II}} \times [\text{Cl}']^a_{\text{II}}$$

from which it is apparent that

$$\frac{[\text{M}^{a+}]_{\text{II}}}{[\text{M}^{a+}]_{\text{I}}} = \frac{[\text{Na}^+]^a_{\text{II}}}{[\text{Na}^+]^a_{\text{I}}} = \frac{x^a}{y^a}$$

Therefore,

$$E = \frac{\text{RT}}{aF} \cdot \log_e \frac{x^a}{y^a} = \frac{\text{RT}}{F} \cdot \log_e \frac{x}{y}$$

This equation shows that, at equilibrium, the unequal distribution of the added ionogen between Solution I and Solution II is producing exactly the same potential difference as the unequal distribution of sodium chloride. Although the addition of any ionogen must produce a change in the measured potential difference, by disturbing the equilibrium, all ionogens present when equilibrium is again established are producing the same potential difference, regardless of valency. The potential difference can

thus be calculated from the determination of the distribution of only one kind of ion between the two solutions.

It should be constantly borne in mind that the complexity of the systems just described is due to the presence of the non-diffusible ion R′ in one of the phases. The equations, which have been derived by recourse only to orthodox physical chemistry, permit one to calculate the effect of the presence of R′ upon the distribution of ions between the two phases and the concomitant osmotic pressure and difference of potential.

The most complete proof of the correctness of Donnan's theory of membrane equilibria has been furnished by Jacques Loeb,[2] who studied the equilibria resulting from the separation of solutions of protein salts from protein-free aqueous solutions by collodion membranes. In this short chapter, it would be impossible to give an adequate description of Loeb's numerous and comprehensive experiments; the reader should consult his book and the files of the *Journal of General Physiology*. (See also Chapter II of this book.) We must be content here with a brief description of only a portion of the work dealing with the Donnan theory.

In his experiments, Loeb used collodion bags which were completely permeable to water and the simpler acids, bases, and salts, but not to dissolved proteins. In order to correlate Loeb's experiments with the Donnan theory just described, let us consider, first of all, a solution of gelatin chloride and hydrochloric acid contained in a collodion bag which is brought into contact with pure water. Hydrochloric acid diffuses out through the membrane until equilibrium is established between the external solution and the gelatin solution inside the bag. The outer solution contains only hydrochloric acid, but the inside solution contains both hydrochloric acid and gelatin chloride. At equilibrium, in the outer solution, let

$$x = [H^+] = [Cl']$$

and in the inside solution let

$$y = [H^+]$$

and $$z = [\text{gelatin ion}^+]$$

whence $$[Cl'] = y + z$$

[2] LOEB, JACQUES: "Proteins and the Theory of Colloidal Behavior," McGraw-Hill Book Co., New York, 1922.

It is apparent from the reasoning given in connection with the Donnan theory that, at equilibrium,

$$x^2 = y(y + z)$$

and that

$$2y + z > 2x$$

The greater concentration of diffusible ions of the inside solution, $2y + z$, must give rise to an osmotic pressure proportional to the quantity e in the expression

$$e = 2y + z - 2x$$

The equations show that x must always be greater than y, or that the concentration of hydrogen ion is greater in the outer solution than in the collodion bag. In numerous experiments, Loeb showed that this is invariably true for acid solutions of gelatin and other proteins. It is also obvious that $2y + z$ is greater than $2x$, or that the concentration of chloride ion is greater in the collodion bag than in the external solution, and this Loeb has also shown to be invariably true. The concentrations of hydrogen ion and chloride ion in both solutions were determined by means of hydrogen and calomel electrodes, respectively. This made it possible to test the validity of the fundamental equation of products.

Table I gives the results of a series of experiments[3] in which 1 per cent solutions of gelatin chloride, acidified to different extents with HCl, were placed in collodion bags immersed in pure water. After 18 hours, equilibrium was established and values for $[H^+]$ and $[Cl']$ were determined both in the gelatin solutions and in the external, protein-free solutions. According to the equation of products, $\log \frac{[H^+]_o}{[H^+]_i}$ must equal $\log \frac{[Cl']_i}{[Cl']_o}$, where o and i indicate concentrations in the outside and inside solutions, respectively. The results show that this equality holds, within the limits of experimental error, over the wide range of pH values from 4.04 to 1.73.

Determinations of osmotic pressure were also found to be in harmony with the Donnan theory. At 24°C., the osmotic pressure, in terms of millimeters pressure of a column of water, equals $250{,}000e$, where e is determined by the expression $2y +$

[3] Loeb, Jacques: *J. Gen. Physiol.*, **3** (1921), 688.

TABLE I

pH or $-\log [H^+]_i$	$\log \frac{[H^+]_o}{[H^+]_i}$	$\log \frac{[Cl']_i}{[Cl']_o}$
4.04	0.60	0.55
3.92	0.62	0.60
3.78	0.66	0.57
3.61	0.55	0.50
3.46	0.50	0.53
3.16	0.43	0.38
2.73	0.30	0.32
2.36	0.20	0.17
2.04	0.12	0.12
1.73	0.07	0.07

$z - 2x$. For both gelatin and casein chlorides, Loeb found that the observed osmotic pressure approximated the values calculated from 250,000e as closely as the accuracy of the determinations of x, y, and z would permit.

By a very ingenious arrangement, Loeb succeeded in measuring the membrane potentials predicted in Donnan's theory. The apparatus used consisted essentially of a pair of saturated calomel electrodes, each having a capillary arm filled with a saturated solution of KCl. The end of one capillary arm was dipped into the gelatin solution in the collodion bag and the end of the other into the external solution. The calomel cells were then connected to a Compton electrometer and the potential difference measured. The potential difference measured was that of the cell

calomel electrode	saturated KCl	external solution	membrane	gelatin solution	saturated KCl	calomel electrode

Everything else being symmetrical, the potential difference measured was that between the external solution and the gelatin solution, across the collodion membrane.

According to the Donnan theory, this potential difference is represented quantitatively by the expression

$$E = \frac{RT}{F} \cdot \log_e \frac{x}{y}$$

As we have pointed out, regardless of the number of kinds of ions present or their valency, in calculating E, we may let x represent the concentration of any monovalent ion in the external solution, and y its concentration in the protein solution. Since the concentration of hydrogen ion lends itself readily to determination, it was selected by Loeb for the purpose. The validity of the equation is proved by the results in Table II. The measurements were made on 1 per cent solutions of gelatin chloride containing different amounts of HCl and enclosed in collodion bags immersed in pure solutions of HCl, each system being in equilibrium at the time the measurements were made. In the above equation, changing from natural to common logarithms and substituting the numerical value for $\frac{RT}{F}$ at 25°C., we get

$$E = 59 \log \frac{x}{y} = 59 (\log x - \log y) \text{ millivolts}$$

where x is the value of $[H^+]$ in the external solution and y its value in the gelatin solution. It is thus rendered possible to get the membrane potential by means of hydrogen electrode

TABLE II

pH value		Potential difference (millivolts)	
Gelatin solution	External solution	By hydrogen electrode	By Loeb's apparatus
4.56	4.14	24.7	24.0
4.31	3.78	31.0	32.0
4.03	3.44	34.5	33.0
3.85	3.26	34.5	32.5
3.33	2.87	27.0	26.0
3.25	2.81	25.8	24.5
2.85	2.53	18.8	16.5
2.52	2.28	14.0	11.2
2.13	2.00	7.6	6.4
1.99	1.89	5.9	4.8
1.79	1.72	4.1	3.7
1.57	1.53	2.3	2.1

measurements as well as by means of Loeb's apparatus just described. Values obtained both ways are given in the table and their close agreement testifies to the correctness of the theory.

We may next consider the effect of adding neutral salts to the gelatin-HCl systems just discussed. Take the mono-monovalent salt MN, neither of whose ions combine with the gelatin, and let its concentration in the external solution, at equilibrium, be represented by u and in the protein solution by v. It is evident from the general equation of products that the product

$$([H^+] + [M^+]) \times ([Cl'] + [N'])$$

will have the same value in both solutions, or that

$$(x + u)^2 = (y + v)(y + v + z)$$

from which it is apparent that

$$e = 2(y + v) + z - 2(x + u)$$

Solving the two preceding equations simultaneously, we get

$$e = -2(x + u) + \sqrt{4(x + u)^2 + z^2}$$

If the values for x and z are kept constant and the value of u increased without limit, it is obvious that the value of e approaches zero as a limit. In other words, by adding to the acid protein system a neutral salt which does not combine with the protein, we bring about a lowering of the value of e with its concomitant lowering of the osmotic pressure and potential difference between the two phases. It is important to recognize that it is the operation of the distribution law and not any supposed repression of ionization of the protein salt that brings about the lowering of the value e.

The correctness of this theory of the action of neutral salts is amply proved by Loeb's experiments. He has also shown that the effect of valency in both acid and alkaline protein systems is quantitatively in accord with the theory we have described for membrane equilibria. Lack of space forces us to refer the reader directly to Loeb's publications.

Jelly Equilibria

When Donnan first published his theory of membrane equilibria, Procter,[4] who was then studying the swelling of gelatin,

[4] Procter, H. R.: *J. Chem. Soc.*, **105** (1914), 313.

recognized that the same fundamental principles apply to the equilibrium between solid gelatin and dilute hydrochloric acid solutions, although jelly equilibria are somewhat more complicated.

When a strip of dry gelatin is soaked in water below 30°C., it swells by absorbing water, increasing in volume from 500 to 1,000 per cent, depending upon the temperature of the water and quality of the gelatin. With increasing concentration of acid or alkali, the swelling increases to a maximum and then decreases. The property of swelling in aqueous solutions appears to be common to all proteins under conditions such that they do not pass directly into solution. The swelling caused by acids and alkalies is generally counteracted by the addition of neutral salt or by increasing the concentration of acid or alkali sufficiently.

While attempting to arrive at a rational explanation of the molecular mechanism of tanning, Procter was continually confronted by the necessity of first explaining the mechanism of the swelling of protein jellies. In 1897 he started an investigation[5] of the swelling of gelatin in solutions of acids and salts which has culminated in the present Procter-Wilson theory of swelling.

Procter's general method of experimentation was as follows: Sheets of thin, purified bone gelatin were cut into portions containing exactly 1 g. each of dry gelatin. A portion was put into each of a series of stoppered bottles containing 100 cc. of hydrochloric acid of definite concentration. After 48 hours, which was shown to be sufficient for the attainment of practical equilibrium, the remaining solution was drained off and titrated with standard alkali. The gelatin plates were quickly weighed and the volume of solution absorbed was calculated from the increase in weight of the plates. The swollen gelatin was then put back into the bottles and covered with enough dry sodium chloride to saturate the solution which had been absorbed by the gelatin. This caused the gelatin to contract and give up the absorbed solution. After 24 hours, when equilibrium was again established, the solution expelled by the salt was drained off and titrated to determine the amount of free acid which had been

[5] Procter, H. R.: *Kolloidchem. Beihefte* (1911); *J. Am. Leather Chem. Assoc.*, **6** (1911), 270.

absorbed by the gelatin. A small amount, usually about 1 cc., of solution always remained unexpelled by the salt and, although not strictly true, this was assumed to have the same concentration of free acid as the portion expelled, due allowance being made for the increase in volume of solution due to saturating it with salt. The acid still unaccounted for was assumed to be combined with the gelatin base.

A further set of checks was obtained by dissolving the gelatin, dehydrated by treatment with salt, in warm water and titrating with standard alkali, using both methyl orange and phenolphthalein, the former indicating the free acid left in the jelly and the latter the total, including the acid combined with the gelatin base, which was obtained by difference.

Procter's experimental results will be considered in connection with the Procter-Wilson theory of swelling[6] now to be discussed. Instead of tracing the development of this theory from Procter's earliest work to its present status, it will simplify matters to present the theory from the deductive reasoning furnished later by Wilson and Wilson.[7] They set out to prove that the entire equilibria can be determined quantitatively from the orthodox laws of physical chemistry on the simple assumption that gelatin, or any other protein, combines with hydrochloric acid to form a highly ionizable chloride, or with any ionogen to form a highly ionizable protein salt. It seemed that success in this would furnish substantial proof of the correctness of the theory. It might be mentioned that Procter's experiments led him very early to the view that gelatin and HCl combine, much in the same manner as do NH_3 and HCl, to form a highly ionizable chloride.

In order to make the reasoning general, let us consider the hypothetical protein G, which is a jelly insoluble in water, is completely permeable to water and all dissolved ionogens considered, is elastic and under all conditions under consideration follows Hooke's law, and combines chemically with the hydrogen ion, but not the anion, of the acid HA according to the equation

$$[G] \times [H^+] = K[GH^+] \qquad (1)$$

[6] Procter, H. R. and Wilson, J. A.: *J. Chem. Soc.*, **109** (1916), 307.
[7] Wilson, J. A. and W. H.: *J. Am. Chem. Soc.*, **40** (1918), 886.

In other words, the compound GHA is completely ionized into GH^+ and A′. The brackets indicate concentration in mols per liter.

Now take 1 millimol of G and immerse it in an aqueous solution of HA. The solution penetrates G, which thereupon combines with some of the hydrogen ions, removing them from solution, and, consequently, the solution within the jelly will have a greater concentration of A′ than of H^+, while in the external solution $[H^+]$ is necessarily equal to [A′]. The solution thus becomes separated into two phases, that within and that surrounding the jelly, and the ions of one phase must finally reach equilibrium with those of the other phase.

At equilibrium, in the external solution, let

$$x = [H^+] = [A']$$

and in the jelly phase let

$$y = [H^+]$$

and $$z = [GH^+]$$

whence $$[A'] = y + z$$

It is apparent from the line of reasoning given earlier in the chapter that the product $[H^+] \times [A']$ will have the same value in both phases at equilibrium, or that

$$x^2 = y(y + z) \tag{2}$$

As was also pointed out above, it is evident from equation (2) that

$$e = 2y + z - 2x \tag{3}$$

where e is defined as the excess of concentration of diffusible ions of the jelly phase over that of the external solution. From (2) and (3) we get

$$x = y + \sqrt{ey} \tag{4}$$

which shows that x is greater than y, or that the hydrogen ion concentration is greater in the external solution than in the jelly. This, in turn, shows that [A′] is greater in the jelly than in the external solution.

Since [A′] is greater in the jelly than in the surrounding solution, the anions of the protein salt will tend to diffuse outward into the external solution, but this they cannot do without

dragging their protein cations with them. These protein cations, however, are not in solution in the generally accepted sense of the word "solution," but form part of an elastic structure which resists the pull of the anions, which are actually in solution. The actual measure of the pull is that of the difference between the total energy directed outward from the jelly and that directed from the external solution towards the jelly. This is obviously represented by the value e and, according to Hooke's law,

$$e = CV \tag{5}$$

where C is a constant corresponding to the bulk modulus of the protein and V is the increase in volume, in cubic centimeters, of 1 millimol of the protein.

Since we have taken 1 millimol of G,

$$[\mathrm{G}] + [\mathrm{GH}^+] = \frac{1}{(V + a)}$$

or

$$[\mathrm{G}] = \frac{1}{(V + a)} - z \tag{6}$$

where a is the initial volume of 1 millimol of the protein.

From (1) and (6)

$$z = \frac{y}{(V + a)(K + y)} \tag{7}$$

and from (2) and (3)

$$z = e + 2\sqrt{ey} \tag{8}$$

From (5) and (8)

$$z = CV + 2\sqrt{CVy} \tag{9}$$

and from (7) and (9)

$$(V + a)(K + y)(CV + 2\sqrt{CVy}) - y = 0 \tag{10}$$

where the only variables are V and y.

If the molecules or atoms of the protein are not themselves permeable to all ions considered, the quantity a should not be taken as the whole of the initial volume of the jelly, but only as the free space within the original, dry jelly through which ions can pass. For our hypothetical protein, then, we shall consider the limiting case where the value of a is zero. This assumption in the case of gelatin introduces errors less than the probable experimental error because of the relatively large values for V

over the significant swelling range. Equation (10) thus reduces to

$$V(K + y)(CV + 2\sqrt{CVy}) - y = 0 \qquad (11)$$

Knowing the values of the constants K and C, we can plot the entire equilibrium as a function of any one variable; given y, we can calculate V from (11); given V, we can calculate e from (5); given y and e, we get z from (8); and we can then get x from (3).

Procter and Wilson obtained the value $K = 0.00015$ for the sample of gelatin used in their experiments by adding successive portions of standard HCl to a dilute solution of the gelatin and noting the corresponding changes in hydrogen ion concentration by means of the hydrogen electrode. The difference between the concentration of hydrogen ion that would have been found upon adding the acid to pure water and that actually found by adding it to the same volume of gelatin solution was taken as the amount of acid combined with the gelatin, or as the value of $[GH^+]$ in equation (1). Substituting any two sets of determinations of $[GH^+]$ and $[H^+]$ in equation (1) and solving the resulting equations simultaneously, the value of K can be found. It is significant that the value for K was determined for gelatin in solution and independently of the swelling experiments.

This left only one constant to be determined from the swelling experiments themselves. C was found by substituting experimental values for V and e in equation (5). It was found to vary with the temperature and with the quality of the gelatin, as would have been expected, but had the value 0.0003 for the gelatin used by Procter at 18°C., the temperature at which his experiments were made.

In order to compare calculated values for V with experimental determinations of the increase in volume of 1 g. of gelatin, it is necessary to know its equivalent weight. Procter originally regarded gelatin as a diacid base with a molecular weight of 839, but later work by Procter and Wilson showed that it should rather be regarded as acting as a monacid base with an equivalent weight of 768, in acid solutions not sufficiently concentrated to cause decomposition. They found that 768 g. of gelatin combine with a limiting value of 1 mol of hydrochloric acid and the combination resembles that of HCl with a weak, monacid base.

For this reason we may use the value 768 as the equivalent weight of gelatin. As for the molecular weight of gelatin, no convincing figures have yet been obtained and it may be questioned whether they would be of any great value anyway. We look upon a plate of gelatin as a continuous network of chains of amino acids, there being no individual molecules, unless one wishes to look upon the entire plate of gelatin as one huge molecule.

By substituting the values $K = 0.00015$ and $C = 0.0003$ in equation (11), Wilson and Wilson were able to calculate all of the variables of the equilibrium for gelatin and HCl over the range covered by Procter's experiments. These are given in Table III along with Procter's actual determinations taken

TABLE III.—AT EQUILIBRIUM

Initial [HCl]	[HCl] in solution	V Calculated	Cubic centimeters of solution absorbed by 1 g. gelatin		[HCl] in jelly		[Total chloride] in jelly	
			Calculated	Observed	Calculated	Observed	Calculated	Observed
0.006	0.0011	33.3	43.4	44.1	0.0001	0.0005	0.012	0.014
0.008	0.0018	37.5	48.8	48.7	0.0002	0.0004	0.014	0.015
0.010	0.0025	41.7	54.3	59.9	0.0004	0.0004	0.016	0.015
0.010	0.0028	42.7	55.6	58.4	0.0004	0.0004	0.017	0.015
0.010	0.0032	43.2	56.2	53.7	0.0005	0.0005	0.019	0.017
0.015	0.0073	40.8	53.1	57.9	0.0020	0.0020	0.024	0.020
0.015	0.0077	40.2	52.3	52.2	0.0020	0.0020	0.025	0.022
0.015	0.0120	37.5	48.8	51.9	0.0050	0.0060	0.031	0.027
0.020	0.0122	37.3	48.6	51.7	0.0050	0.0060	0.031	0.027
0.025	0.0170	34.5	44.9	40.4	0.0080	0.0090	0.036	0.037
0.025	0.0172	34.3	44.7	48.1	0.0080	0.0090	0.036	0.031
0.050	0.0406	26.7	34.8	36.4	0.0260	0.0300	0.063	0.061
0.050	0.0420	26.4	34.4	31.1	0.0270	0.0300	0.065	0.068
....	0.0576	24.0	31.2	34.0	0.0410	0.0430	0.082	0.079
0.075	0.0666	23.0	29.9	27.9	0.0490	0.0500	0.092	0.095
0.075	0.0680	22.8	29.7	29.1	0.0500	0.0530	0.094	0.092
0.100	0.0930	20.7	27.0	23.1	0.0720	0.0720	0.121	0.126
0.100	0.0944	20.5	26.7	26.4	0.0730	0.0720	0.122	0.121
....	0.1052	19.8	25.8	29.8	0.0830	0.0850	0.134	0.128
0.125	0.1180	18.9	24.6	24.4	0.0950	0.0900	0.148	0.148
0.150	0.1434	17.9	23.3	24.0	0.1180	0.1180	0.174	0.173
0.150	0.1435	17.9	23.3	24.2	0.1180	0.1180	0.174	0.172
0.175	0.1685	17.1	22.3	23.5	0.1410	0.1380	0.200	0.200
0.200	0.1925	16.3	21.2	20.6	0.1640	0.1610	0.225	0.229
0.200	0.1940	16.2	21.1	22.7	0.1660	0.1650	0.227	0.225
0.200	0.1945	16.2	21.1	22.1	0.1670	0.1640	0.228	0.226
0.250	0.2450	15.1	19.7	20.2	0.2130	0.2100	0.279	0.281
0.300	0.2950	14.0	18.2	20.0	0.2610	0.2600	0.332	0.332

from the table on page 317 of his 1914 paper.[8] They are also shown graphically in Figs. 1 and 2, in which the concentration of gelatin chloride is taken as the difference between the concentrations of total chloride and free hydrochloric acid in the jelly. It will be noted that the agreement between calculated and observed values is absolute, within the limits of experimental

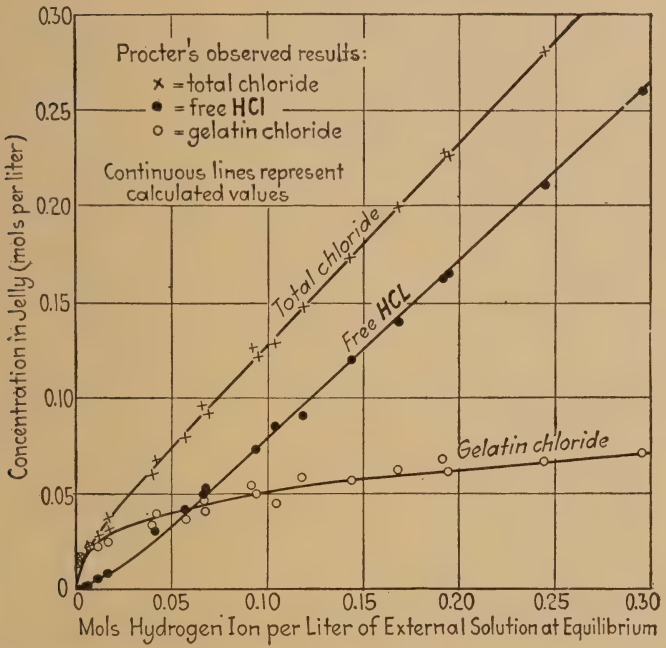

FIG. 1.—Observed and calculated values for the distribution of HCl in the system gelatin-HCl-water.

error. For this reason the theory may be regarded as proved. It is worthy of note that no other theory of the swelling of jellies has yet passed the stage of qualitative speculation.

According to the theory, all monobasic acids should produce the same degree of swelling of a given protein for any fixed hydrogen ion concentration, under constant conditions, provided the protein salts formed are ionized to the same extent. It was formerly thought that different monobasic acids produce different

[8] PROCTER, H. R.: *J. Chem. Soc.*, **105** (1914), 313.

degrees of swelling, following the order known as the Hofmeister series of the ions, but Loeb and Kunitz[9] showed that earlier investigators, through failure to measure the hydrogen ion concentration, had fallen into the error of attributing to the several acids effects caused merely by differences in hydrogen ion concentration. For a fixed value of x, they obtained the same degree

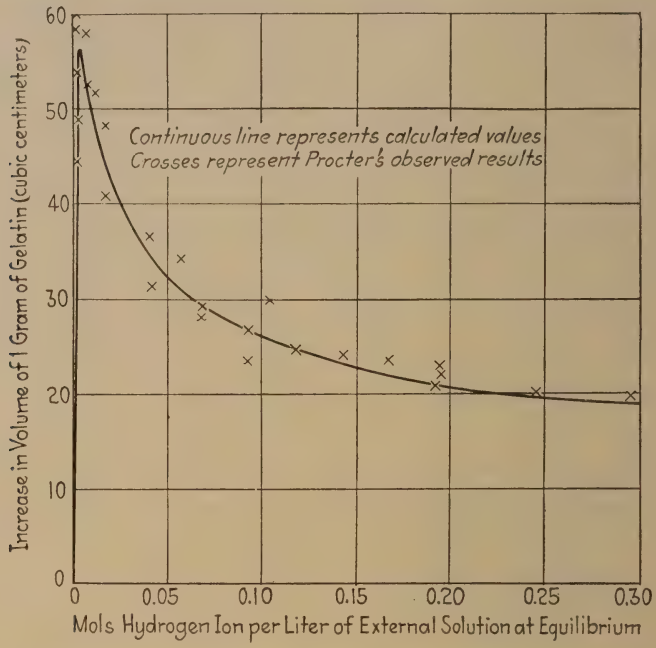

FIG. 2.—Observed and calculated values for he degree of swelling of gelatin as a function of the concentration of hydrochloric acid in the external solution at equilibrium.

of swelling of gelatin with all monobasic acids studied as well as with such acids as phosphoric and oxalic at concentrations at which they act as monobasic.

The extent of swelling of proteins by polybasic acids, which combine as such with the protein, will, according to the theory, be considerably less than that caused by monobasic acids at the same hydrogen ion concentration, because a smaller total number of anions will be associated with equivalent weights of the protein.

[9] LOEB, J. and KUNITZ, M.: *J. Gen. Physiol.*, **5** (1923), 665.

For example, for equivalent weights of gelatin sulfate and gelatin chloride, there would be only half as many sulfate as chloride ions. For very small values of x, we should, therefore, expect sulfuric acid to produce only half the degree of swelling produced by hydrochloric acid at the same value of x, and Loeb has repeatedly shown this to be true.

It will be apparent from the discussion of membrane equilibria that the value of e in the case of acid-swollen jellies also will be lowered by the addition of neutral salts which do not combine with the protein. This means a decrease in swelling, which is in perfect harmony with all experimental data.

It is also apparent that there must be a measurable difference of potential between the jelly phase and the external solution; this has actually been measured by Loeb and found to be in quantitative agreement with the theory.

Surface Equilibria

It was pointed out by the present writer[10] in 1916 that at the surface of contact between an aqueous solution and any electrically charged solid there must exist an equilibrium of the type just described for jellies. As an example, we may consider a gold sol. As has been shown by Beans and Eastlack,[11] when gold is dispersed in water, the presence of chloride, bromide, iodide, or hydroxide ion in concentrations ranging from 0.00005 to 0.005 normal has a marked stabilizing effect on the sol produced and the particles are negatively charged. The effect seems to be due to the ability of these ions to form stable compounds with the gold. Fluoride, nitrate, sulfate, and chlorate ions decrease the stability of gold sols, which is significant in view of the fact that they do not form stable compounds with gold.

Let us consider any single particle of gold in a sol stabilized with potassium chloride. In combining with the gold, the chloride ions have imparted their negative charges to the particle. But the potassium ions are still left in solution, although their field of motion is restricted to the thin film of solution wetting

[10] Wilson, J. A.: *J. Am. Chem. Soc.*, **38** (1916), 1982.

[11] Beans, H. T. and Eastlack, H. E.: *J. Am. Chem. Soc.*, **37** (1915), 2667.

the particles, because they must continue to balance the negative charges on the particle. The volume of the film of aqueous solution enveloping the particle will be measured by the surface area of the particle and the average distance that the potassium ions are free to travel from the oppositely charged surface. The enveloping film of solution will contain more potassium ions than chloride ions, since it contains ionized potassium chloride as well as potassium ions balanced only by the negative charges on the surface of the gold particle. In the solution far removed from the surface of the particle, potassium and chloride ions will be present in equal numbers.

The distribution of ions here described shows a striking analogy to the distribution of ions between a jelly and the surrounding solution. In the case of the jelly, the system consisted of the following three phases: the solid protein network, the solution between the interstices of the network, and the solution surrounding the jelly mass. In the case of the gold sol, we also have three phases: the solid surface, the film of solution wetting the surface, and the great bulk of solution further removed from the surface of the particle.

To show the analogy still more clearly, let us adopt a similar system of notation and in the bulk of solution of the gold sol let

$$x = [K^+] = [Cl']$$

In the enveloping film of solution wetting the particles, let

$$y = [Cl']$$

and $z = [K^+]$, balancing the charges on the particles, whence $y + z$ represents the total concentration of potassium ion.

It is immediately apparent that our equation of products applies to the distribution of ions between the bulk of solution and that portion wetting the particles, or that

$$x^2 = y(y + z)$$

The surface film of solution will have a greater total concentration of ions than the surrounding solution by the amount $2y + z - 2x$. This unequal distribution of ions will give rise to an

electrical difference of potential between the enveloping film and the surrounding solution whose measure is

$$E = \frac{RT}{F} \log_e \frac{x}{y} = \frac{RT}{F} \log_e \frac{2x}{-z + \sqrt{4x^2 + z^2}}$$

But now, if we increase the value of x without limit, while z remains constant, E must decrease, approaching zero as a limit, since

$$\lim_{x = \infty} E = \frac{RT}{F} \log_e \frac{2x}{\sqrt{4x^2}} = 0$$

It is thus evident that the difference of potential between the enveloping film and the surrounding solution will be a maximum when there is no free potassium chloride present and will decrease, approaching zero, as the concentration of potassium chloride is increased without limit. The writer believes that the electrostatic repulsion opposing the coalescence of the particles is determined by this potential difference rather than by the absolute electrical charge on the particles because the surface film completely envelops the particles and tends to endow them with its own properties.

When enough potassium chloride has been added to lower the potential difference to a point where it is no longer able to overcome the attractive forces between the particles and the surface tension of the enveloping film, the particles move toward each other and the enveloping films of two or more particles blend into one. It is at this point that the actual charges themselves come into play and probably determine the nature of the precipitate. It should be noted that the lowering of the potential difference between the enveloping film and surrounding solution does not necessarily involve any lowering whatsoever of the value of the electrical charge on the particle itself. It is also apparent that the theory holds just as well regardless of the actual cause of the charge on the particles. We have thus an explanation of the precipitation of sols by the addition of electrolyte.

Discussion of the theory of heterogeneous equilibria presented in this chapter might be continued indefinitely, but it is hoped that enough has been given to show that the well-known distribu-

tion law may become a powerful tool in clearing up many of the mysteries of colloid chemistry, once the phase boundaries in the systems studied are clearly recognized. Further discussions of many of the points presented in this chapter may be found in the recent books of Loeb,[12] Bogue,[13] Procter,[14] and the writer.[15]

[12] Loeb, Jacques: "Proteins and the Theory of Colloidal Behavior," McGraw-Hill Book Co., New York, 1922.

[13] Bogue, Robert Herman: "Chemistry and Technology of Gelatin and Glue," McGraw-Hill Book Co., New York, 1922.

[14] Procter, Henry Richardson: "Principles of Leather Manufacture," D. Van Nostrand Co., New York, 1922.

[15] Wilson, John Arthur: "The Chemistry of Leather Manufacture," The Chemical Catalog Co., New York, 1923.

CHAPTER II

CRYSTALLOIDAL AND COLLOIDAL BEHAVIOR OF PROTEINS

By

JACQUES LOEB

THE CRYSTALLOIDAL BEHAVIOR OF PROTEINS

Chemical Behavior.—The treatment of the subject of colloidal behavior has in many cases not yet risen above the level of mere qualitative speculations. This is chiefly due to the fact that many of the authors of colloidal literature have failed to measure and to consider one of the main variables in their experiments, namely, the hydrogen ion concentration of their solutions or gels. If this quantity is duly measured and taken into consideration, the subject of colloidal behavior can be raised above the mere qualitative state and based upon a quantitative basis, which permits the derivation of the observed results from a rationalistic formula without the use of arbitrary constants. It is the intention of this article to show that this is true at least for one group of colloids, the proteins, the colloidal behavior of which can be explained quantitatively from Donnan's theory of so-called membrane equilibria.[1]

[1] The following books are recommended for general reference to the physical chemistry of proteins:

MICHAELIS, L.: "Die Wasserstoffionenkonzentration," 1st ed. Berlin, 1914; 2nd ed., vol. 1, Berlin, 1922.

ROBERTSON, T. B.: "The Physical Chemistry of the Proteins," New York, 1918.

SÖRENSEN, S. P. L.: "Studies on Proteins," *Compt.-rend. trav. lab. Carlsberg*, vol. 12, Copenhagen, 1915–17.

PAULI, W.: "Colloid Chemistry of Proteins," New York, 1922.

BOGUE, R. H.: "Chemistry and Technology of Gelatin and Glue," New York, 1922.

WILSON, J. A.: "The Chemistry of Leather Manufacture," New York, 1923.

LOEB, J.: "Proteins and the Theory of Colloidal Behavior," New York, 1922. (Referred to hereafter briefly as "Proteins.")

The distinction between crystalloids and colloids was proposed by Graham in 1861, the crystalloids being characterized by a tendency to form crystals when separating from an aqueous solution, and the colloids by a tendency to separate out in the form of "gelatinous" (or amorphous) masses. Graham found that these two groups of substances differ also in other respects, first, in their "diffusive mobility," and, second, in a peculiar "physical aggregation." The crystalloids diffuse readily through many kinds of membranes (*e.g.*, pig's bladder, parchment) through which colloids can diffuse not at all or only very slowly. The second peculiarity is the tendency of the colloids to form aggregates when in solution, while this property is lacking or less pronounced in crystalloids. A brief quotation from a paper by Graham will illustrate these definitions:

> Among the latter [*i.e.*, the substances with low order of diffusibility] are hydrated silicic acid, hydrated alumina, and other metallic peroxides of the aluminous class, when they exist in the soluble form; and starch, dextrin and the gums, caramel, tannin, albumen, gelatin, vegetable and animal extractive matters. Low diffusibility is not the only property which the bodies last enumerated possess in common. They are distinguished by the gelatinous character of their hydrates. Although often largely soluble in water, they are held in solution by a most feeble force. They appear singularly inert in the capacity of acids and bases, and in all the ordinary chemical relations. But, on the other hand, their peculiar physical aggregation with the chemical indifference referred to, appears to be required in substances that can intervene in the organic processes of life. The plastic elements of the animal body are found in this class. As gelatin appears to be its type, it is proposed to designate substances of the class as *colloids*, and to speak of their peculiar form of aggregation as the *colloidal condition of matter*. Opposed to the colloidal is the crystalline condition. Substances affecting the latter form will be classed as *crystalloids*. The distinction is no doubt one of intimate molecular constitution.[2]

It is, therefore, obvious that there are, according to Graham, at least two essential differences between colloids and crystalloids, the difference in diffusion through membranes, and the difference in the tendency to form aggregates in solutions. Both properties play a rôle in colloidal behavior, but they determine

[2] GRAHAM, T.: *Phil. Trans.* (1861), 183–224. Reprinted in "Chemical and Physical Researches," p. 553, Edinburgh, 1876.

different colloidal properties, as will be shown in the case of proteins.

Recent investigations on proteins have yielded the result that the distinction between crystalloids and colloids is no longer tenable. It was found that proteins behave like crystalloids in regard to chemical combination, solubility, cohesion, and possibly some other properties; and that they show colloidal behavior only under one well-defined condition, namely, when the large protein ions are prevented from diffusing through membranes or gels which are readily permeable to the small ions of ordinary salts.[3]

It is known through the work of Emil Fischer that the proteins are built up from amino acids in peptide linkage. The amino acids are amphoteric electrolytes and true crystalloids, being able to diffuse freely through dialyzing membranes such as parchment, and showing true solubility in water. Like the amino acids, proteins are also amphoteric electrolytes capable of combining both with acids and alkalies and forming true salts which undergo electrolytic dissociation.[4] Whether proteins combine with acids or with alkalies depends on the hydrogen ion concentration. At a certain hydrogen ion concentration, which varies with each individual protein (according to the amino acids of which it is composed), the protein combines with neither acid nor alkali, and this critical hydrogen ion concentration is called the *isoelectric point.* When the hydrogen ion concentration of a protein solution is greater than that of the isoelectric point, *i.e.*, when the solution is on the acid side from the isoelectric point, the protein forms salts of the type of protein chloride, protein sulfate, etc., while, when the hydrogen ion concentration is less than that of the isoelectric point, the protein forms salts of the type of metal proteinates, such as sodium proteinate, calcium proteinate, and so on. In the following the hydrogen ion concentration of protein solutions or protein gels is expressed in terms

[3] Loeb, J.: "Proteins," New York, 1922, and a series of articles in the *Journal of General Physiology*, vols. 1 to 5.

[4] Bugarszky, S. and Liebermann, L.: *Arch. ges. Physiol.*, **72** (1898), 51; Robertson, T. B.: "The Physical Chemistry of the Proteins," New York, 1918; Hardy, W. B.: *J. Physiol.*, **33** (1905-06), 251; Pauli, W.: *Fortschr. naturwiss. Forschung*, **4** (1912), 223; "Kolloidchemie der Eiweisskörper," Dresden and Leipzig, 1920; Loeb, J.: "Proteins," New York, 1922.

of Sörensen's logarithmic symbol, pH (pH being the negative logarithm of the hydrogen ion concentration).

A protein solution or gel is not adequately defined unless its pH has been measured. When a salt, *e.g.*, $AgNO_3$, is added to

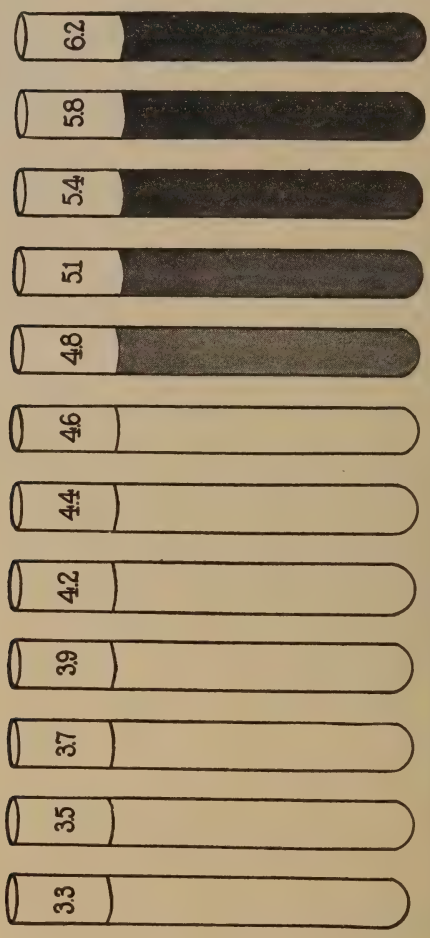

FIG. 1.—Proof that cations combine with proteins only on the alkaline side of the isoelectric point. Powdered gelatin brought to different pH was treated in a dark room with M /64 $AgNO_3$ and then washed with cold water to remove the silver not in combination with gelatin. The gelatin was liquefied, brought to a 1 per cent solution, and the pH was determined. The solutions were then poured into test-tubes and exposed to light. In about half an hour the gelatin of pH >4.7 was dark while the gelatin of pH 4.7 or less remained permanently clear though exposed to light for over a year. The pH of each gelatin solution is marked at the head of each test-tube.

finely powdered gelatin at different pH, it is found that Ag gelatinate can be formed only when the pH is greater than 4.7 (this being the isoelectric point of gelatin); and when $K_4Fe(CN)_6$ is

added, gelatin ferrocyanide can be formed only when the pH is less than 4.7 (Figs. 1 and 2). This can be shown by methods described in a recent book.[5]

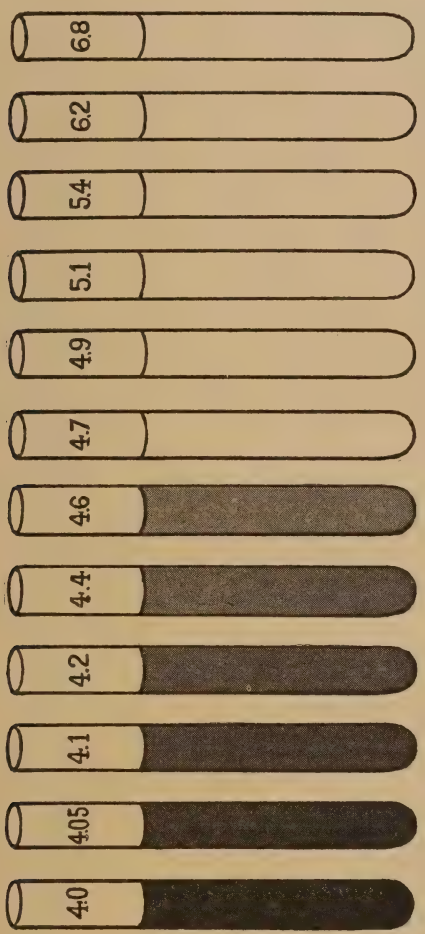

FIG. 2.—Proof that anions combine with proteins only on the acid side of the isoelectric point. Doses of powdered gelatin solutions of different pH were treated with M/128 $K_4Fe(CN)_6$ and then washed with cold water. All the samples of gelatin solution of pH<4.7 turned blue—in this figure indicated in black—(through the formation of some ferric salt), while all the gelatin solutions of pH 4.7 or above remained colorless.

The proof that proteins combine stoichiometrically with acids and alkalies can be furnished by titration and combination curves. For this purpose (and perhaps for work with proteins in general) it is necessary to use, as standard material, protein of the pH

[5] LOEB, J.: "Proteins," p. 28.

of the isoelectric point. We have seen that proteins combine with acids only at a pH below that of the isoelectric point, which for gelatin or casein is about pH 4.7, and for crystalline egg albu-

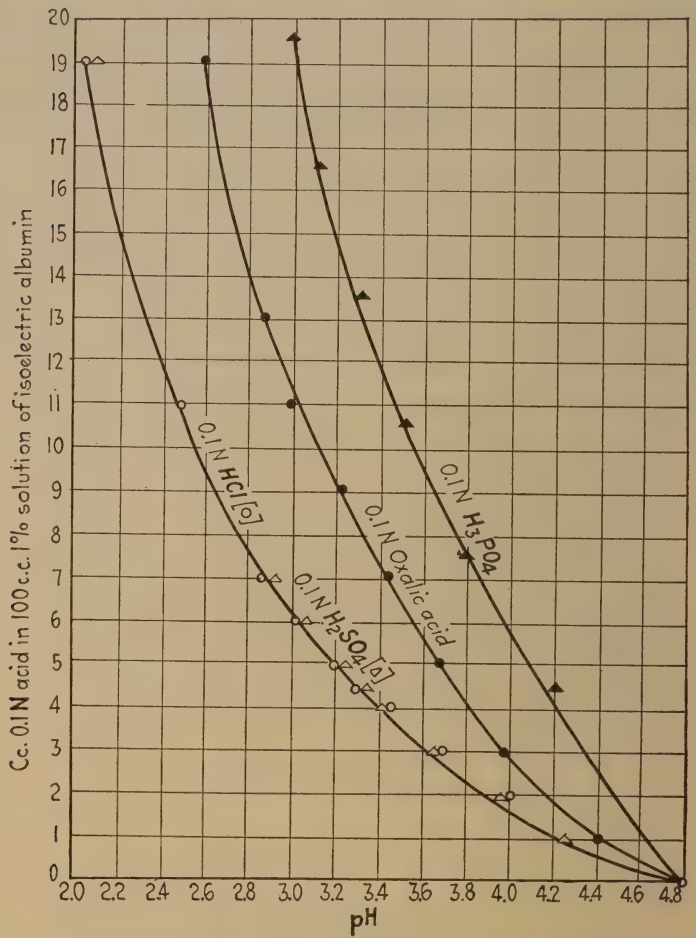

FIG. 3.—The ordinates represent the number of cubic centimeters of 0.1 N HCl, H_2SO_4, oxalic, and phosphoric acids required to bring 1 g. of isoelectric crystalline egg albumin to the pH indicated on the axis of abscissæ. Enough H_2O was added to bring the albumin and acid to a volume of 100 cc. For the same pH the ordinates for HCl, H_2SO_4, and phosphoric acid are approximately as 1:1:3. The ratio of HCl to oxalic acid is a little less than 1:2, when pH is >3.0.

min 4.8. It happens that at a pH below 4.7 most of the weak dibasic and tribasic acids dissociate as monobasic acids. Thus,

H_3PO_4 dissociates into H^+ and the monovalent anion $H_2PO_4^-$. Hence, if acids combine stoichiometrically with isoelectric protein, it should require exactly three times as many cubic centimeters of 0.1 N H_3PO_4 to bring a 1 per cent solution of an isoelectric protein, *e.g.*, gelatin or crystalline egg albumin or casein, to the same hydrogen ion concentration, *e.g.*, pH 3.0, as it requires of 0.1 N HCl or HNO_3. Titration experiments show that this is the case. Furthermore, since H_2SO_4 is a strong acid, splitting off both hydrogen ions even at a pH below 4.7, the same number of cubic centimeters of 0.1 N H_2SO_4 as of HCl should be required to bring 1 g. of isoelectric protein in 100 cc. of solution to the same pH, *e.g.*, 3.0, and this was found also to be true.

Figure 3 gives the titration curves for crystalline egg albumin for four acids, HCl, H_2SO_4, H_3PO_4, and oxalic acid. One gram of isoelectric albumin was dissolved in 100 cc. of H_2O containing varying amounts of 0.1 N acid. These cubic centimeters of 0.1 N acid in 100 cc. solution are the ordinates of the curves in Fig. 3. The abscissæ are the pH to which the protein solution was brought by the addition of acid. It takes always exactly three times as many cubic centimeters of 0.1 N H_3PO_4 as it takes cubic centimeters of 0.1 N HCl or H_2SO_4 to bring 1 g. of isoelectric albumin in 100 cc. of solution to the same pH. In order to bring the 1 per cent solution of originally isoelectric albumin to pH 3.2, 5 cc. of 0.1 N HCl or H_2SO_4 and 15 cc. of 0.1 N H_3PO_4 must be contained in 100 cc. of the solution. To bring the albumin to pH 3.4, 4 cc. of 0.1 N HCl or H_2SO_4 and 12 cc. of 0.1 N H_3PO_4 must be contained in the solution, and so on.

Oxalic acid is, according to Hildebrand, a monobasic acid at a pH of 3.0 or below, but begins to split off the second hydrogen ion in increasing proportion above pH 3.0. The titration curves show that about twice as many cubic centimeters of 0.1 N oxalic acid as 0.1 N HCl are required to bring the 1 per cent solution of isoelectric albumin to the same pH below 3.0, while it takes less than twice as many cubic centimeters of 0.1 N oxalic acid as 0.1 N HCl to bring the albumin solution to the same pH if the pH is above 3.0.

All this in itself would not yet prove that proteins combine stoichiometrically with acids and alkalies, but this proof is furnished if we calculate the amount of acid in actual combina-

tion with a given mass of protein. From the titration curves, the amount of acid in combination with 1 g. of originally isoelectric protein, *e.g.*, crystalline egg albumin, in a 1 per cent solution of this protein at different pH can easily be calculated. Let us assume the acid added to isoelectric albumin to be HCl. If, *e.g.*, at pH 3.0, 6 cc. of 0.1 N HCl are contained in 100 cc. of the 1 per cent solution of the originally isoelectric albumin (as indicated in Fig. 3), part of the acid is in combination with the albumin and part is free. How much is free is known from the pH of the albumin chloride solution, namely, 1 cc., since in the example selected the pH is 3.0 (Fig. 3).

If 1 cc. is deducted from 6 cc., it is found that, at pH 3.0, 5 cc. of 0.1 N HCl are in combination with 1 g. of originally isoelectric crystalline egg albumin in 100 cc. solution. A curve is constructed in which the abscissæ are the pH while the ordinates are the cubic centimeters of free 0.1 N HCl contained in 100 cc. of an aqueous solution as expressed by the pH of the solution. If the ordinates of this latter curve are deducted from the ordinates of the titration curve in Fig. 3, we get a curve the ordinates of which give the number of cubic centimeters of 0.1 N HCl in actual combination with 1 g. of originally isoelectric albumin in 100 cc. of solution.

The results in Table I show the actual numbers of cubic centimeters of 0.1 N solutions of each of the four acids in combination with 1 g. of originally isoelectric crystalline egg albumin in 100 cc. of solution. The values for HCl and H_2SO_4 are identical. Those for H_3PO_4 are within the limits of the accuracy of the measurements, always three times as large as those for HCl.

In the case of oxalic acid, we notice that at pH above 3.6 the number of cubic centimeters of 0.1 N oxalic acid in combination with 1 g. of albumin is less than twice that of HCl and that the difference is greater the higher the pH. At pH 3.2 and below, practically twice as many cubic centimeters of oxalic acid are, at the same pH, in combination with 1 g. of originally isoelectric albumin as there are of HCl. These titration experiments then leave no doubt that 1 g. of originally isoelectric albumin binds the same number of H ions at a given pH regardless of whether the acid added is a moderately weak acid like H_3PO_4 or oxalic acid or a strong acid like HCl or H_2SO_4.[6] That these

[6] Loeb, J.: "Proteins," p. 44; *J. Gen. Physiol.*, **1** (1918–19), 559; **3** (1920–21), 85.

TABLE I.—CUBIC CENTIMETERS OF 0.1 N ACID IN COMBINATION WITH 1 G. OF ORIGINALLY ISOELECTRIC CRYSTALLINE EGG ALBUMIN IN 100 CC. OF SOLUTION

pH	HCl, cc.	H_2SO_4, cc.	Oxalic acid, cc.	H_3PO_4, cc.
4.2	1.15	1.15	1.8	3.8
4.0	1.70	1.70	2.6	5.3
3.8	2.30	2.30	3.7	6.8
3.6	2.90	2.90	5.0	8.6
3.4	3.50	3.50	6.3	10.6
3.2	4.20	4.30	8.0	13.1
3.0	5.00	5.10	9.5	16.1
2.8	5.80	5.90	11.1	19.3
2.6	6.70	6.50	13.3	22.9
2.4	7.60	7.00	16.0	

simple facts had not been discovered earlier is the consequence of the failure of the workers to measure the hydrogen ion concentration of their solutions. Had this been done, nobody would have thought of suggesting that acids combine with proteins according to the adsorption formula.

The same proof was furnished by the writer for the combination of gelatin and casein[7] and by Hitchcock for edestin and serum globulin.[8] It shows that no matter whether a weak or strong acid is added to bring a given mass of isoelectric gelatin to the same pH, the same number of hydrogen ions is in combination with the protein. This is the expression of a purely stoichiometrical behavior and the simplest assumption is that the hydrogen ion of the acid is bound chemically by the protein.

It can be shown with the aid of titration curves that isoelectric albumin combines with alkalies in the same stoichiometrical way as any acid, *e.g.*, acetic acid, would combine with the same alkalies. If the cubic centimeters of 0.1 N KOH, NaOH, $Ca(OH)_2$, or $Ba(OH)_2$ in 100 cc. of solution required to bring a 1 per cent solution of isoelectric protein to the same pH are plotted as ordinates over the pH of the protein solution as abscissæ, it is

[7] LOEB, J.: "Proteins."

[8] HITCHCOCK, D. I.: *J. Gen. Physiol.*, **4** (1921–22), 597; **5** (1922–23), 35.

found that the values for all four alkalies fall on one curve as they should if the combination occurred strictly stoichiometrically.

The stoichiometrical character of the combination of proteins with hydrochloric acid can also be demonstrated by measuring the chlorine ion concentration of the solutions of protein chloride. When HCl is added to NH_3 (according to Werner) the H ions of the HCl are attracted to the nitrogen of the ammonia, while the Cl ions remain unaltered. The same type of reaction occurs when HCl is added to a solution of isoelectric gelatin. This was proved by measurements of the pCl of solutions of gelatin chloride. Different numbers of cubic centimeters of 0.1 N HCl were contained in 100 cc. of 1 per cent solutions of originally isoelectric gelatin and the pH and pCl of the solutions were measured, the pH with the hydrogen electrode and the pCl with the calomel electrode. It was found that the pCl was the same as if no gelatin had been present, while the pH was, of course, higher, thus showing that part of the hydrogen combines with the NH_2 and NH groups of the protein molecule while the Cl remains free (Table II).[9]

TABLE II

Cubic centimeters of 0.1 N HCl in 100 cc. solution	Solution containing no gelatin		Solution containing 1 g. of isoelectric gelatin in 100 cc.	
	pH	pCl	pH	pCl
2	2.72	2.72	4.20	2.680
3	2.52	2.54	4.00	2.530
4	2.41	2.39		
5	2.31	2.29	3.60	2.330
6	2.24	2.26	3.41	2.250
7	2.16	2.18	3.23	2.180
8	2.11	2.12	3.07	2.110
10	2.01	2.01	2.78	2.025
15	1.85	1.85	2.30	1.845
20	1.72	1.76	2.06	1.760
30	1.55	1.59	1.78	1.600
40	1.43	1.47	1.61	1.470

[9] LOEB, J.: "Proteins," p. 42.

Hitchcock[10] has obtained similar results with crystalline egg albumin, edestin, casein, and serum globulin, by using a silver-silver chloride electrode, so that it is possible to state that these results are true for many if not all proteins. These measurements show that a protein chloride dissociates electrolytically into a large protein cation and a number of chlorine ions. A similar conclusion had already been reached by Manabe and Matula,[11] and by Pauli[12] on the basis of measurements of the pCl of gelatin and serum albumin chloride solutions.

The titration curves prove another fact, namely, that the salts of proteins are strongly hydrolyzed. When we add acid, *e.g.*, HCl, to isoelectric protein, part of the acid combines with the protein, giving rise to protein chloride, while the rest of the acid remains free. There is then an equilibrium between free HCl, protein chloride, and non-ionogenic (or isoelectric) protein. The more acid is added to originally isoelectric protein, the more protein chloride is formed, until finally all the protein exists in the form of protein chloride. This point is reached for gelatin chloride at pH 2.5. It is possible to find out from the pH measurements how much of the acid added is free, and by deducting this value we know how much is in combination with the protein. By saturating the protein with acid, the combining weight of a protein with acid can be found. Hitchcock[13] found in this way that the combining weight of gelatin is about 1,120. According to Dakin's[14] recent analyses, gelatin contains 1.4 per cent phenylalanine. Since 1 molecule of gelatin cannot contain less than 1 molecule of phenylalanine, and since the molecular weight of this amino acid is 165, the lowest possible weight of gelatin is 11,800. On this basis 1 molecule of gelatin should combine with 10 or a multiple of 10 hydrogen ions.

Cohn and Hendry[15] calculated from the titration curve of casein with sodium hydroxide a combining weight of about 2,100 for casein. Dakin found about 1.7 per cent of tryptophane in

[10] Hitchcock, D. I.: *J. Gen. Physiol.*, **5** (1922–23), 383.
[11] Manabe, K. and Matula, J.: *Biochem. Z.*, **52** (1913), 369.
[12] Pauli, W.: "Colloid Chemistry of Proteins," New York, 1922.
[13] Hitchcock, D. I.: *J. Gen. Physiol.*, **6** (1923–24), 95.
[14] Dakin, H. D.: *J. Biol. Chem.*, **44** (1920), 499.
[15] Cohn, E. J. and Hendry, J. L.: *J. Gen. Physiol.*, **5** (1922–23), 548.

casein and, according to this, the molecular weight of casein must be 12,000 (or a multiple thereof). This would indicate that 6 or a multiple of 6 hydroxyl ions combine with 1 molecule of casein. Cohn and Hendry point out that the calculation of the molecular weight of casein from sulfur and phosphorus contents agrees also with the molecular weight estimated from the titration curves.

Minimal molecular weight of casein calculated from tryptophane (average)	12,800
Minimal molecular weight of casein calculated from phosphorus × 3	13,116
Minimal molecular weight of casein calculated from sulfur × 3	12,654
Equivalent combining weight of casein for sodium hydroxide × 6	12,600
Average	12,792

All these data are difficult to understand on any other assumption than that proteins combine stoichiometrically with acid and alkali and that we are dealing with true chemical combination.

A new proof that the combination of proteins with acids is true chemical combination, following the ordinary laws of classical chemistry, has recently been added by Hitchcock.[16] Deaminized gelatin was prepared by treating gelatin with nitrous acid, following the procedure of Skraup. Determinations were made of the total nitrogen in gelatin and in deaminized gelatin, by the Kjeldahl method, and of the amino nitrogen in gelatin, by the Van Slyke method. It was found that the loss of total nitrogen in gelatin which had been deaminized by Skraup's method was greater than the amino nitrogen originally present in the gelatin. Accordingly, the procedure of Skraup was modified by avoiding the application of heat in preparing the deaminized gelatin. The resulting product was found to have undergone a loss in total nitrogen exactly equal to the amino nitrogen originally present, indicating that under these conditions the deaminizing reaction really consisted simply in the replacement of amino groups by hydroxyl groups.

In order to determine the combining capacity of deaminized gelatin for hydrochloric acid, it was necessary to ascertain its isoelectric point. This was done by measurements of the osmotic pressure developed at different pH values, following the procedure used by Loeb with other proteins. The minimum of osmotic

[16] Hitchcock, D. I.: *J. Gen. Physiol.*, **6** (1923–24), 95.

pressure, and, hence, the isoelectric point of the protein, was found to be at pH 4.0.

Finally, the combining capacity of the protein for hydrochloric acid was determined by electrometric titration with the hydrogen electrode, following a procedure similar to that previously used with gelatin and other proteins. It was found that the difference between the maximum combining capacities of gelatin and of deaminized gelatin for hydrochloric acid was approximately equivalent to the free amino nitrogen originally present in the gelatin and removed in the deaminizing reaction. Thus the work constitutes a new type of evidence that the reactions of proteins with acid are truly chemical and stoichiometric.

Solubility of Proteins.—It has been generally assumed in colloidal literature that colloids in general and proteins in particular cannot form true aqueous solutions, *i.e.*, solutions in which the ultimate unit is a protein ion or a protein molecule. Instead, it was assumed that proteins form only suspensions in which the ultimate unit is an aggregate of molecules or ions, a so-called micelle. The forces responsible for true solutions are entirely different from the forces responsible for the stability of suspensions. While the stability of the isolated molecules or ions in true solutions is determined by the strong forces of attraction between molecules or ions of solute and water, the stability of solid aggregates (micelles) in water is determined by the weak forces of repulsion due to the electrical double layer between each particle and water. When the potential difference (P.D.) of this electrical double layer falls below a critical value (which is about 16 millivolts for collodion particles in water)[17] the particles will coalesce upon colliding, and settle rapidly. Low concentrations of neutral salts suffice to bring the P.D. between the particles and water below the critical limit, causing flocculation. Schulze,[18] Picton and Linder,[19] and Hardy[20] have shown that the flocculating effect of a salt increases rapidly with the increasing valency

[17] Loeb, J.: *J. Gen. Physiol.*, **5** (1922–23), 109.

[18] Schulze, H.: *J. prakt. Chem.*, **25** (1882), 431; **27** (1883), 320; **32** (1884), 390.

[19] Picton, H. and Linder, S. E.: *J. Chem. Soc.*, **61, 67, 71, 87.**

[20] Hardy, W. B.: *Proc. Roy. Soc.*, **66** (1900), 110; **79** (1907), 413; *J. Physiol.*, **29** (1903), 29; **33** (1905–06), 251; Wood, T. B. and Hardy, W. B.: *Proc. Roy. Soc.*, **81** (1909), 38.

of that ion of the salt which is charged oppositely to the particles moving in an electrical field. It requires generally, however, high concentrations of salts to cause precipitation of molecules and ions from true solution and the precipitating ion of the salt has not necessarily a charge opposite to that of the suspended particle. When this criterion is applied to solutions of genuine proteins, *e.g.*, crystalline egg albumin or gelatin, it is found that they form true solutions, since enormous concentrations of salts are required to precipitate these proteins from their solutions and since, moreover, the sign of charge of the active ion of the salt is not opposite to that of the protein. Sulfates precipitate solutions of gelatin better than chlorides, no matter whether the protein is at the isoelectric point or on the acid side of the isoelectric point or on the alkaline side (see Table III).[21] Such results are incompatible with the idea that the forces which keep protein in solution are the weak repulsive forces due to electrical double layers.

TABLE III.—MINIMAL MOLAR CONCENTRATIONS REQUIRED TO PRECIPITATE 0.8 PER CENT SOLUTIONS OF GELATIN

pH of gelatin solution	Approximate molecular concentration of salt required for precipitation				
	$(NH_4)_2SO_4$	Na_2SO_4	$MgSO_4$	KCl	$MgCl_2$
4.7 (isoelectric gelatin)..	15/16 M	6/8 M	10/8 M	>3 M	>3 M
3.8 (gelatin chloride).....	13/16 M	5/8 M	7/8 M	3 M	>3 M
6.4 to 7.0 (Na gelatinate).	16/16 M	7/8 M	9/8 M	>3 M	>3 M

The only alternative is that these forces are the strong forces responsible for true solubility. The direct quantitative proof that proteins possess true solubility like any crystalloid was furnished by Cohn and Hendry[22] in an investigation of the relation between the solubility of casein and its capacity to combine with a base. This investigation was based on the principle of the constancy of the solubility product. It was found by these authors that

[21] LOEB, J.: "Proteins," p. 245.

[22] COHN, E. J. and HENDRY, J. L.: *J. Gen. Physiol.*, **5** (1922–23), 521.

casein forms a well-defined soluble disodium compound and that solubility was completely determined by (1) the solubility of the casein molecule, and (2) the concentration of the disodium casein compound. From the study of systems containing the protein and very small amounts of sodium hydroxide it was possible to determine the solubility of the casein molecule and also the degree to which it dissociated as a divalent acid and combined with base. Solubility in such systems increased in direct proportion to the amount of sodium hydroxide they contained. The concentration of the soluble casein compound varied inversely as the square root of the hydrogen ion concentration, directly as the solubility of the casein molecule, and as the constants Ka_1 and Ka_2 defining its acid dissociation. These investigations leave no doubt that the solubility of casein is adequately characterized as a true crystalloidal solubility. There is also little doubt that this result can be applied to all genuine proteins.

Two apparent difficulties have to be removed. Hardy, who had discovered the existence of the isoelectric point of protein particles in his famous experiments on the migration of particles of denatured egg albumin in an electrical field, had also noticed that the stability of suspensions of boiled white of egg was a minimum at the isoelectric point, and he ascribed this correctly to the fact that the cataphoretic P.D. between particles and water is a minimum at this point.[23] This explanation cannot be applied, however, to aqueous solutions of genuine proteins, such as crystalline egg albumin, gelatin, etc. The solubility of genuine proteins in water is also a minimum at the isoelectric point and increases as a rule when alkali or acid is added, but for a different reason; namely, because protein salts and amphoteric electrolytes in general are more soluble in water than the non-ionized molecules. Since the ionization of proteins is a minimum at the isoelectric point, their solubility must also be a minimum at this point. This was pointed out already by Michaelis,[24] and Michaelis and Davidsohn[25] have shown that this is also true for amino acids, which are true crystalloids.

[23] HARDY, W. B.: *Loc. cit.*

[24] MICHAELIS, L.: "Die Wasserstoffionenkonzentration," Berlin, 1914, p. 44.

[25] MICHAELIS, L. and DAVIDSOHN, H.: *Biochem. Z.*, **30** (1910), 143.

The second apparent difficulty lies in the fact that certain proteins, *e.g.*, gelatin, form micelles on standing. When a solution of gelatin is left standing, it will set to a gel, if the concentration of gelatin is not too low, and the formation of a continuous gel is naturally preceded by the formation of smaller aggregates. But the formation of gels does not contradict the fact that the forces which keep gelatin in solution are those forces of attraction between the molecules or ions of gelatin and water which determine the true solubility of crystalloids like amino acids or any other substance, and which are designated by Langmuir as forces of secondary valency. On the basis of the well-known ideas developed by Langmuir and by Harkins it is necessary to distinguish in the case of large molecules between the relative affinity of each group of the molecule for water and for each other. Thus hydrocarbon groups are attracted more powerfully to each other than by water, and groups like NH_2 or NH_3^+ or COOH are attracted more strongly by water than by each other. Gelatin molecules or ions are dragged into the water by their NH_2 or NH_3^+ and COOH or COO^- groups, but they are attracted to each other by their hydrocarbon groups. When two molecules of gelatin happen to come in contact with two hydrocarbon groups, they may remain attached to each other without any weakening of the attractive force between their NH_2 or COOH groups and water. In a gel of gelatin the average distance between gelatin molecules is the same as in a gelatin solution; what is changed is only the orientation of the gelatin molecules towards each other.[26]

That the colloid chemists overlooked the fact that proteins possess true solubility is again the consequence of their failure to measure properly the hydrogen ion concentration of their solutions. Without such measurements it is, of course, impossible to prove the validity of the principle of the solubility product for proteins, or to prove that the active ion in salting out of proteins may have the same sign of charge as the protein ion. It is, therefore, no mere accident that all those authors who have measured the hydrogen ion concentrations of protein solutions, such as Michaelis and his follow workers, Sörensen,[27] E. J. Cohn,

[26] Loeb, J.: "Proteins," p. 243.

[27] Sörensen, S. P. L.: *Compt.-rend. trav. lab. Carlsberg*, **12** (1915–17), 6.

and the writer, have reached the conclusion that proteins form true solutions.

The Colloidal Behavior of Proteins

Membrane, Equilibria and Their Equations.—If proteins behave like crystalloids, chemically and in regard to solubility, the question may be asked: Why are proteins termed colloids? The answer is that proteins show colloidal behavior only in regard to the influence of electrolytes on four well-defined properties, namely, membrane potentials, osmotic pressure, swelling, and that form of viscosity which is due to the swelling of submicroscopic particles. This influence of electrolytes is similar on all four properties and may be summarized in the following way:

1. The addition of little acid or alkali to isoelectric protein increases at first the value of these four properties until a maximum is reached, after which the addition of more acid or alkali diminishes the value of these properties again.

2. This influence of acids and alkalies depends only on the valency, and not upon the chemical nature of the anion of the acid or the cation of the alkali. It is, *e.g.*, the same for all acids the anions of which are monovalent, provided the effects of different acids on the four properties mentioned are compared at the same pH of the protein solution or protein gel.

3. When the anion of the acid or the cation of the alkali is bivalent (*e.g.*, SO_4, Mg, Ca, Ba, etc.), the membrane potentials, osmotic pressure, viscosity, and swelling of the protein are considerably less than when the ion is monovalent (*e.g.*, Cl, Br, NO_3, H_2PO_4, HC_2O_4, Li, Na, K, NH_4, etc.).

4. The addition of a neutral salt to a protein solution or protein gel (not at the isoelectric point) depresses the value of the four properties and this depressing effect increases with the valency of that ion of the salt which has the opposite sign of charge to that of the protein ion. The chemical nature of the active ion of the salt has no direct influence on these four properties but may affect some of them, *e.g.*, swelling or viscosity, indirectly by influencing the cohesion of a gel or its solubility.

No such influence of electrolytes is observed on amino acids or on other typical crystalloids, and the question arises: Which peculiarity of the proteins gives rise to this specific influence of electro-

lytes on the four properties mentioned? The answer is that the peculiarity in question is the large protein ion which is prevented from diffusing through many membranes or through gels easily permeable to the smaller ions of the ordinary crystalloidal electrolytes. This selective diffusion is the basis of the method of dialysis as well as of a peculiar equilibrium condition whereby the concentration of the diffusible ions is, at equilibrium, not the same inside a protein solution and in an outside aqueous solution, free from protein, separated by a dialyzing membrane. This unequal distribution of the diffusible ions on the opposite sides of a dialyzing membrane separating a protein solution and an aqueous solution free from protein, when equilibrium is established between the two solutions, is the sole cause of the peculiar influence of electrolytes on the four properties of proteins, and, hence, the sole cause of the colloidal behavior of proteins. The theory of such membrane equilibria has been developed by Donnan.

Suppose a collodion bag of a volume of about 50 cc. is filled with a solution of gelatin chloride of pH 3.0, containing 1 g. of originally isoelectric gelatin in 100 cc. of solution. The bag is closed with a rubber stopper perforated by a glass tube serving as a manometer. The collodion bag is submerged in 350 cc. of a solution of HCl originally also of pH 3.0. Water will diffuse into the gelatin solution, the level of water rising in the manometer until finally a definite level is reached which will remain constant. This level is the hydrostatic pressure at which the system is in osmotic equilibrium. The equilibrium is established at 24°C. after about 6 hours, but it is better to wait 18 hours before measurements are taken. It is found that when equilibrium is established, the concentration of the H and Cl ions is not the same inside the gelatin solution and in the outside aqueous solution.[28]

The gelatin chloride solution inside the bag is dissociated into gelatin ions and Cl ions. The molar concentration of the latter may be designated as z. In addition, there exists free HCl inside the gelatin chloride solution due to hydrolytic dissociation of the gelatin salt as shown by the titration and combination curves. Let y be the molar concentration of the H and of the Cl

[28] Loeb, J.: "Proteins," p. 169; *Science*, **56** (1922), 731.

ions of the free HCl inside the gelatin solution at equilibrium. Then the total molar concentration of H ions inside the protein solution at equilibrium is y and that of the Cl ions $y + z$.

Let x be the molar concentration of the H and Cl ions in the outside solution at osmotic equilibrium. Since it can be shown experimentally that the collodion membrane is impermeable to the solution of most if not all proteins, but perfectly permeable to H and Cl ions, at osmotic equilibrium the distribution of H and Cl ions on the opposite sides of the membrane must be determined by Donnan's equation for membrane equilibria, according to which the products of the molar concentrations of each pair of oppositely charged ions must be equal on the opposite sides of the membrane, *i.e.*, in the case of gelatin chloride solutions,

$$x^2 = y(y + z) \qquad (1)^{29}$$

This equation is the same for all acids with monovalent anion. When the anion is bivalent, the equilibrium equation is one of the third degree; namely,

$$x^3 = y^2(y + z) \qquad (2)^{30}$$

where $\frac{z}{2}$ is the molar concentration of the anion in combination with the gelatin. Only the valency but not the chemical nature of the anion of the acid enters, therefore, into the equations for the Donnan equilibrium.

Membrane Potentials.—To 1 g. dry weight of isoelectric gelatin were added different numbers of cubic centimeters of 0.1 N solutions of various acids, HCl, HBr, HI, HNO_3, acetic acid, etc., and the total volume was brought to 100 cc. by the addition of

[29] Donnan, F. G.: *Z. Elektrochem.*, **17** (1911), 572; Lewis, W. C. McC.: "A System of Physical Chemistry," vol. 2, p. 399, London, 1920; Procter, H. R. and Wilson, J. A.: *J. Chem. Soc.*, **109** (1916), 307; Loeb, J.: "Proteins"; *J. Gen. Physiol.*, **3** (1920–21), 667, 691, 827; **4** (1921–22), 73, 97; Bogue, R. H.: "The Chemistry and Technology of Gelatin and Glue," New York, 1922, p. 128; Wilson, J. A.: "The Chemistry of Leather Manufacture," New York, 1923, p. 94.

[30] Loeb, J.: "Proteins," p. 120; *J. Gen. Physiol.*, **3** (1920–21), 667; **4** (1921–22), 351, 769; Loeb, J. and Kunitz, M.: *J. Gen. Physiol.*, **5** (1922–23), 665.

distilled water. Collodion bags of about 50-cc. content were filled with these protein solutions and each bag was closed with a rubber stopper perforated by a glass tube serving as a manometer. Each bag was put into 350 cc. of water free from protein but containing some of the same acid as that added inside to the gelatin. This was done to hasten the establishment of equilibrium. After 18 hours the height of the column of H_2O in the glass tube was measured (giving the osmotic pressure of the protein solution), and the P.D. was then determined between the protein solution and the outside aqueous solution by means of a Compton electrometer with two saturated KCl-calomel electrodes. The e.m.f. of the following cell was, therefore, measured:

Hg	HgCl	saturated KCl solution	gelatin acid solution +	collodion membrane	outside aqueous solution −	saturated KCl solution	HgCl	Hg

This e.m.f. will be called the membrane potential. Figure 4 gives the results. The abscissæ are the pH of the protein solutions at equilibrium (determined with the hydrogen electrode) and the ordinates are the P.D. measured with the electrometer. First it is noticeable that the membrane potentials are a minimum at the isoelectric point, that they rise with diminishing pH (*i.e.*, increasing hydrogen ion concentration) until a maximal P.D. is reached at about pH 4.0, and that with a further diminution of the pH the potentials fall again.[31]

That the membrane potentials are due to the Donnan equilibrium follows from the following facts:

1. The values for the influence of all the acids with monovalent anion, HCl, HBr, HI, HNO_3, acetic, propionic, and lactic acids, on the membrane potential between gelatin solution and outside aqueous solution lie on one curve (Fig. 4). The values representing the influence of the two strong dibasic acids, H_2SO_4 and sulfosalicylic acid, on membrane potentials lie also on one curve (Fig. 4), but this curve is lower than that for the monobasic acids.[32] The chemical nature of the anion plays no rôle, as Donnan's equation demands, since the membrane equilibria

[31] LOEB, J.: "Proteins," p. 122; LOEB, J. and KUNITZ, M.: *J. Gen. Physiol.*, **5** (1922–23), 671.

[32] LOEB, J. and KUNITZ, M.: *J. Gen. Physiol.*, **5** (1922–23), 671.

are purely electrostatic equilibria depending only on the number of charges but not on the chemical nature of the ions. No other physical properties, except those due to the Donnan equilibrium,

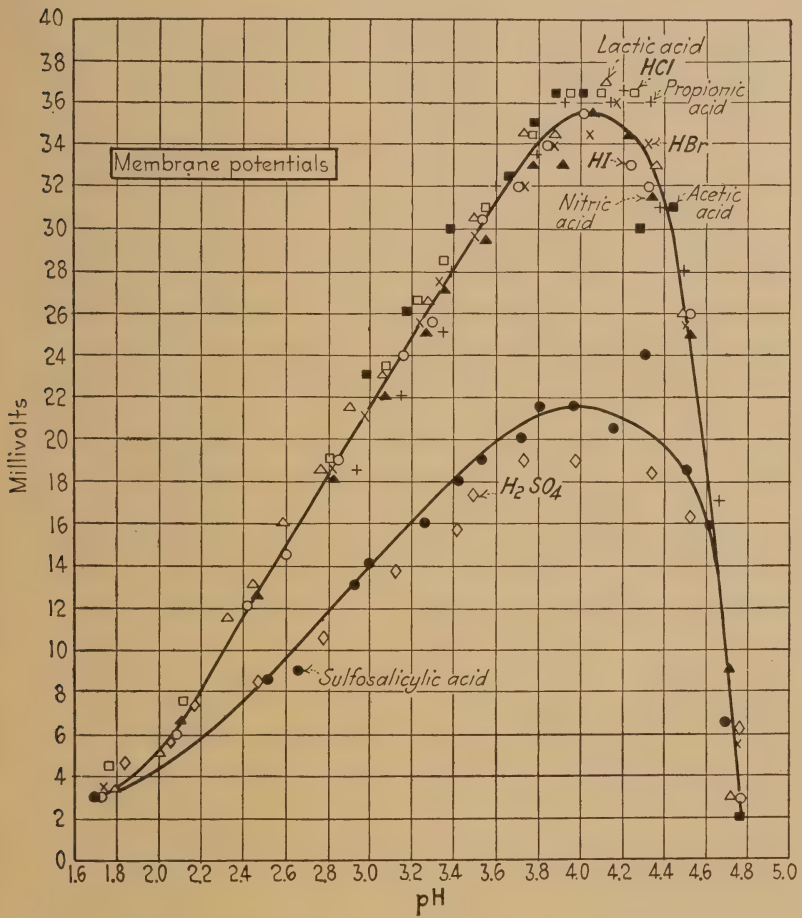

FIG. 4.—Proof that only the valency of the anion of an acid influences the membrane potentials of gelatin solutions. The ordinates are the membrane potentials in millivolts; the abscissæ the pH of gelatin solutions. The membrane potentials of the seven monobasic acids are practically identical and so are the membrane potentials of the two strong dibasic acids.

show this peculiarity, that only the valency but not the chemical nature of the ion has any effect on the colloidal properties.

2. Donnan's equilibrium equation for monobasic acids can be written in the form

$$\frac{x}{y} = \frac{y+z}{x}$$

Donnan has shown that there must exist between the inside and outside solution a P.D. as follows:

$$\text{P.D.} = \frac{RT}{F} \log_e \frac{x}{y}$$

where x is the molar concentration of hydrogen ions outside, and y the molar concentration of hydrogen ions inside. Since pH outside is $-\log x$ and pH inside $-\log y$, the membrane potential measured with the indifferent calomel electrodes should be equal to the hydrogen electrode potential between the gelatin solution and the outside aqueous solution, if Donnan's membrane equilibria are the cause of the membrane potentials. This was found to be true within the limits of the accuracy of the measurements (about 2 millivolts). By hydrogen electrode potentials is understood the value 59 × (pH inside minus pH outside) millivolts, where each pH is measured between a calomel-saturated KCl electrode and a hydrogen electrode. What was actually measured was the difference in the e.m.f. of the following two cells:

(*a*)

H_2	inside gelatin chloride solution	saturated KCl	HgCl	Hg

(*b*)

H_2	outside aqueous solution	saturated KCl	HgCl	Hg

In Fig. 5 are given the hydrogen electrode potentials of the same acids as in Fig. 4. The curves for the hydrogen electrode P.D. in Fig. 5 and the curves for the membrane P.D. in Fig. 4 are identical. The hydrogen electrode P.D.'s for all the monobasic acids are, therefore, the same within the limits of accuracy of measurements and the P.D.'s for the two strong dibasic acids are also the same in both Figs. 4 and 5.

3. Loeb had shown furthermore that if Donnan's membrane equilibrium is responsible for the effect of acids on the membrane potentials of protein solutions, the effects of monobasic acids

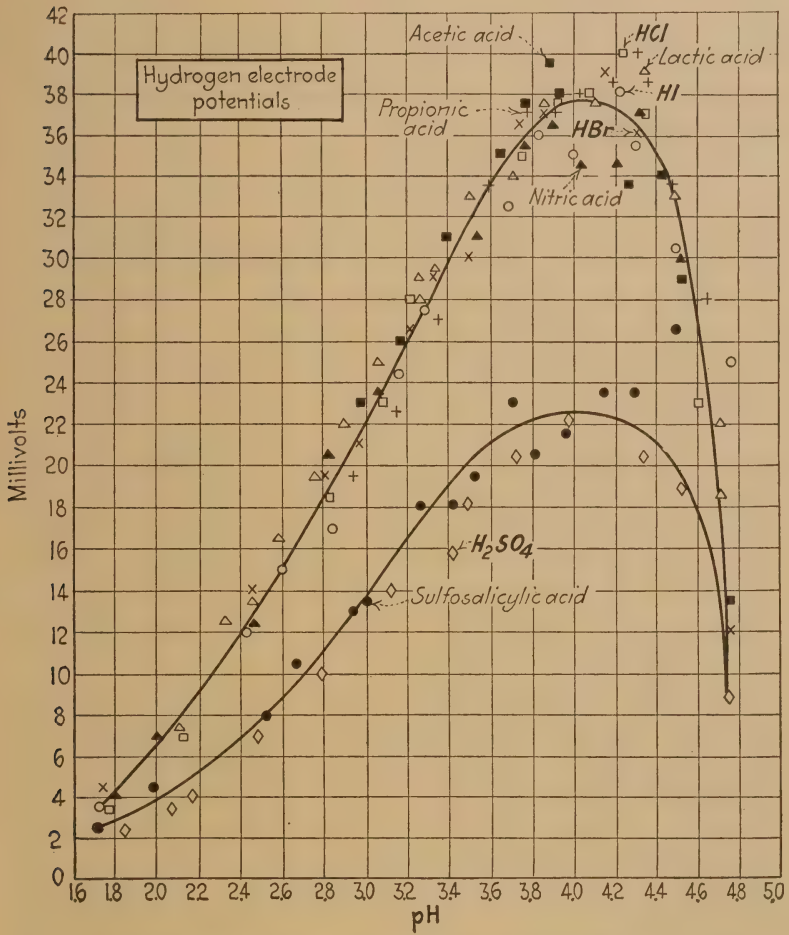

FIG. 5.—Proof that the influence of acids on the hydrogen electrode potentials of gelatin solutions is identical with that on the membrane potentials as shown in Fig. 4.

should be exactly 50 per cent higher than those for dibasic acids at the same pH on the basis of the following consideration.

From equation (1) it follows that in the case of monobasic acids $x = \sqrt{y(y+z)}$. Substituting this value for x in the term $\frac{x}{y}$, we get

$$\frac{\sqrt{y(y+z)}}{y} = \sqrt{\frac{y+z}{y}} = \sqrt{1+\frac{z}{y}}$$

Hence, the membrane potential of a protein solution should be at 24° for monobasic acids

$$\text{P.D.} = \frac{58}{2}\log\left(1+\frac{z}{y}\right)\text{millivolts}$$

From equation (2) it follows that in the case of dibasic acids

$$x = \sqrt[3]{y^2(y+z)}$$

Substituting this value in $\frac{x}{y}$ we get

$$\frac{x}{y} = \frac{\sqrt[3]{y^2(y+z)}}{y} = \sqrt[3]{\frac{y^2(y+z)}{y^3}} = \sqrt[3]{\frac{y+z}{y}} = \sqrt[3]{1+\frac{z}{y}}$$

The P.D. is, therefore, in the case of a dibasic acid

$$\text{P.D.} = \frac{58}{3}\log\left(1+\frac{z}{y}\right)\text{millivolts}$$

Hence, at the same pH of the gelatin solution the ratio of the P.D. of gelatin sulfate over that of gelatin chloride must be as 2:3, or 0.66.[33]

A comparison of the effects of sulfosalicylic acid with those for HCl and the other monobasic acids at the same pH in Fig. 5 shows that this is correct within the limits of experimental accuracy (Table IV).[34]

The values for sulfosalicylic acid were used in preference to the values for sulfuric acid, for the reason that a repetition of the experiment with sulfuric acid showed that the values for sulfosalicylic and sulfuric acids are, in reality, identical, and that the values for sulfuric acid given in Fig. 4 are a little too low.

Most weak dibasic and tribasic acids dissociate as monobasic acids below a certain pH. H_3PO_4 dissociates as monobasic acid

[33] LOEB, J.: "Proteins," p. 132.

[34] LOEB, J. and KUNITZ, M.: *J. Gen. Physiol.*, **5** (1922–23), 675.

TABLE IV.—MEMBRANE POTENTIALS FOR DIBASIC AND MONOBASIC ACIDS

pH	Dibasic acids, millivolts	Monobasic acids, millivolts	Ratio $\frac{\text{dibasic}}{\text{monobasic}}$
2.4	7.6	11.4	0.67
2.6	9.6	14.8	0.65
2.8	11.6	18.0	0.64
3.0	13.6	21.6	0.65
3.2	15.8	24.8	0.64
3.4	18.0	28.0	0.62
3.6	19.8	31.0	0.64
3.8	21.2	34.2	0.62
4.0	21.6	35.5	0.61
4.2	20.8	34.8	0.60
4.4	19.2	31.0	0.62

below pH 4.7 and it had been shown that in this range of pH the influence of H_3PO_4 on membrane potentials (as well as osmotic pressure, swelling, and viscosity) is identical with that of HCl or any other monobasic acid if compared for the same pH of the protein solution or gel. Oxalic acid dissociates as a monobasic acid below pH 3.0 and it had been shown that for pH of 3.0 or less the influence of the oxalic acid on the properties mentioned is like that of HCl. Above pH 3.0 the second H ion of the oxalic acid begins to dissociate and the relative number of dibasic anion increases with a further increase of pH and, hence, the depressing effect of the dibasic anion is felt more and more the higher the pH.[35]

After these remarks, the effect of succinic, citric, and tartaric acids on the membrane potentials as plotted in Fig. 6 is easily understood. All three acids act like HCl below pH 3.0, *i.e.*, the curve representing the influence of these three acids on the membrane potential coincides with that for HCl, but not with that for H_2SO_4, which means that all these acids dissociate for pH < 3.0 as monobasic acids, and, furthermore, it is clear that these weak dibasic acids behave as the valency rule demands.

[35] LOEB, J.: "Proteins," pp. 122, 127.

Above pH 3.0 the curves for succinic, citric, and tartaric acids are lower than the curve for HCl but considerably higher than that for H_2SO_4, which means that at a pH > 3.0 the second H ion of the weak dibasic and tribasic acids begins to be split off,

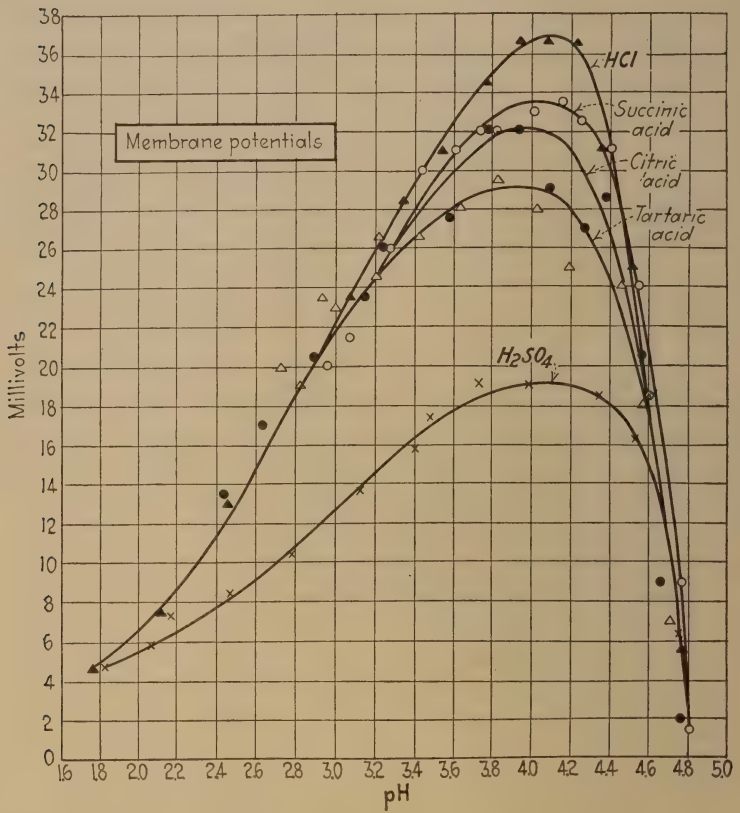

FIG. 6.—Influence of weak dibasic and tribasic acids on the membrane potentials of gelatin solutions.

and the more, the stronger the acid. Thus, in the case of the weak succinic acid only a very small percentage of molecules dissociates as dibasic acid and the same may be said for citric acid, while a greater percentage of tartaric acid molecules dissociates as dibasic acid between pH 3.0 and 4.7. These

experiments might almost be used as a criterion for the mode of dissociation of weak dibasic and tribasic acids.[36]

4. The term P.D. $= \frac{58}{2} \log \left(1 + \frac{z}{y}\right)$ gives also an explanation of why the addition of little acid to isoelectric gelatin increases the membrane potentials until a maximum is reached, after which the addition of more acid diminishes the P.D. again. The addition of acid to originally isoelectric protein increases the value of z, *i.e.*, the concentration of ionized protein acid salt, as well as the value of y, *i.e.*, the concentration of anion; but at first z increases more rapidly than y, until a certain percentage of protein is ionized when, with the addition of more acid, the value of z increases less rapidly than that of y.[37]

5. It is also obvious from the above term for the P.D. why a salt can only depress but cannot raise the P.D. The addition of a salt cannot increase the value of z, *i.e.*, the concentration of ionized protein, while with the increase in the concentration of the salt the value of y, *i.e.*, the anion of the protein salt, will increase.[38]

6. The membrane potentials as measured by the two indifferent calomel electrodes must also be equal to the chlorine ion potentials if the membrane equilibria are the cause of the P.D., and the writer's measurements have shown this to be true within the limits of the accuracy of the measurements.[39]

7. The value of the membrane potentials must increase with the concentration of the protein in solution, since this increases the value of z in equations (1) and (2), and this was also found to be correct.[40]

These facts leave no doubt that the influence of electrolytes on the membrane potentials between protein solutions and outside aqueous solutions can be explained quantitatively from Donnan's theory of membrane equilibria.

Osmotic Pressure of Protein Solutions.—The same experiments which were used for the measurement of membrane poten-

[36] LOEB, J. and KUNITZ, M.: *J. Gen. Physiol.*, **5** (1922–23), 677.
[37] LOEB, J.: "Proteins," p. 131.
[38] *Ibid.*: p. 143.
[39] *Ibid.*: p. 135.
[40] *Ibid.*: p. 145.

tials were also used for measuring the osmotic pressure of gelatin solutions containing 1 g. dry weight of originally isoelectric gelatin in 100 cc. of water made up with various acids. The results are contained in Fig. 7. The ordinates are the observed osmotic

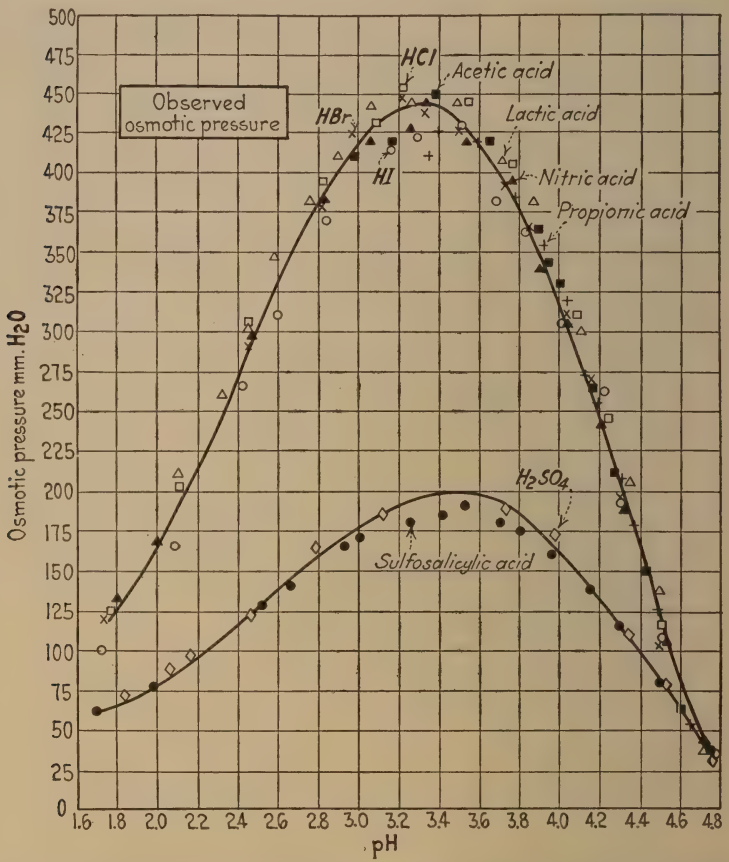

FIG. 7.—Proof of valency rule for the influence of acids on the osmotic pressure of gelatin solutions. The influence of seven monobasic acids on the osmotic pressure of gelatin solutions is the same and about twice as high as that of the two dibasic acids.

pressures in terms of millimeters of a column of water, and the abscissæ are the pH of the gelatin solution at equilibrium. It is obvious that the osmotic pressure of the gelatin solution is a minimum at the isoelectric point, that it rises upon the addition

of acid until a maximum is reached at pH 3.3, and that, upon the further addition of acid, the osmotic pressure diminishes again. It is also noticeable that all the monobasic acids influence the osmotic pressure in exactly the same way; and the values for

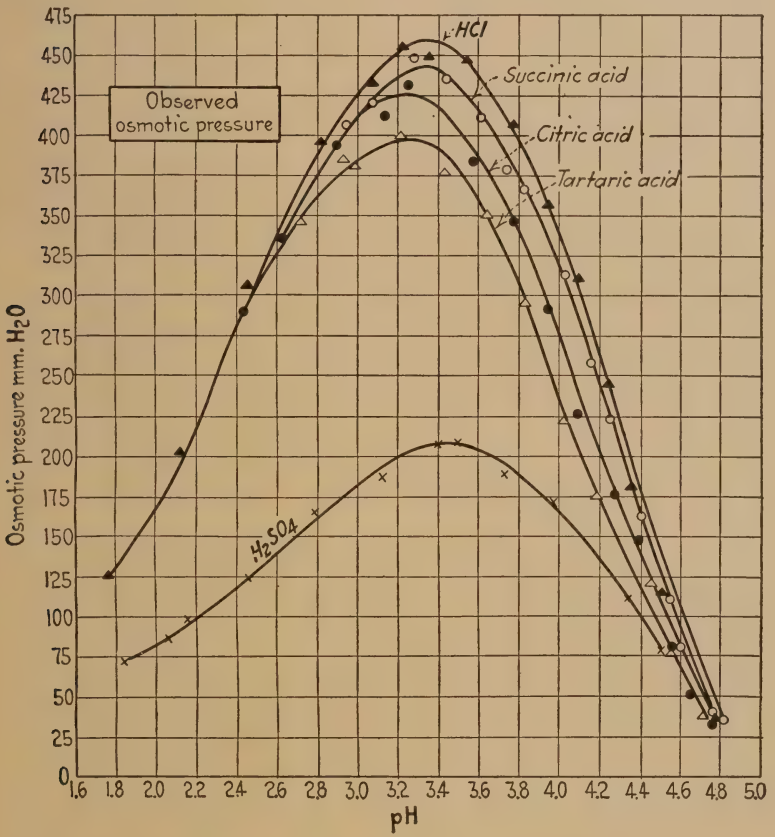

FIG. 8.—Influence of weak dibasic and tribasic acids on the osmotic pressure of gelatin solutions.

HCl, HBr, HI, HNO_3, acetic, propionic, or lactic acids lie practically all on one curve. The osmotic pressure curves for the two strong dibasic acids, H_2SO_4 and sulfosalicylic acid, also fall on one curve, which is, however, entirely different, being about half as high as the curve for the monobasic acids for the same pH.[41]

[41] *Ibid.*: p. 169; LOEB, J. and KUNITZ, M.: *J. Gen. Physiol.*, **5** (1922–23) 665.

It had been shown in preceding papers and in a book that the curve representing the influence of H_3PO_4 on the osmotic pressure of a gelatin solution is identical with the curve representing the influence of HCl, if both are plotted over the pH of the gelatin solution as abscissæ; and that the curve for oxalic acid is also identical with the curve for HCl and H_3PO_4 for pH 3.0 or below, while for pH above 3.0 the influence of the bivalent oxalate anion becomes noticeable in the fact that the osmotic pressure for oxalic acid is, in that range of pH, lower than for HCl.[42]

Figure 8 represents the influence of succinic, citric, and tartaric acids on the osmotic pressure of a solution containing 1 g. dry weight of originally isoelectric gelatin in 100 cc. solution. As was to be expected, the descending branches of the curves for these acids are identical with the corresponding part of the curve for HCl for pH below 3.0, while above pH 3.0 the curves for the three weak dibasic or tribasic acids are slightly lower in the order of their relative strength as discussed in connection with the membrane potentials.[43]

It would be possible to use the influence of dibasic or tribasic acids on the osmotic pressure of protein solutions to determine their relative strengths.

Now the question arises: What causes this influence of acids on osmotic pressure? First, the fact shown in Figs. 7 and 8, that only the valency but not the chemical nature of the anion of the acid influences the osmotic pressure, is to be expected if this influence of the acid is due to the Donnan equilibrium. An equally important task is, however, to explain why the addition of little acid raises and why the addition of more acid depresses again the osmotic pressure. The colloid chemists would have taken it for granted that such curves were due to an influence of the acids on the state of dispersion or on some other real or imaginary colloidal property of proteins. Before we have a right to indulge in such speculations, we must realize that these curves of observed osmotic pressure are not exclusively the expression of the osmotic pressure due to the protein particles, protein molecules, and protein ions alone, but are also the result of the demonstrable unequal concentrations of the crystalloidal ions on the opposite sides of

[42] Loeb, J.: "Proteins," p. 174.

[43] Loeb, J. and Kunitz, M.: *Loc. cit.*

the membrane, caused by the establishment of a Donnan equilibrium. In other words, the observed osmotic pressure of a protein solution needs a correction due to the Donnan equilibrium before we can begin to speculate on the cause of the influence of acid on these curves, and it is our purpose to calculate the value of this correction.

We begin with the curve expressing the influence of HCl on the osmotic pressure of a 1 per cent solution of originally isoelectric gelatin and we consider the distribution of ions inside the protein solution and in the aqueous solution outside the collodion bag containing the protein solution at osmotic equilibrium. We also assume complete electrolytic dissociation of gelatin chloride as well as HCl. Let a be the molar concentration of the protein molecules and ions, let z be the molar concentration of the Cl ions in combination with the ionized protein, let y be the molar concentration of the hydrogen ions of the free HCl inside the protein solution; the molar concentration of the Cl ions of this HCl is also y. In that case the osmotic pressure of the protein solution is determined by the molar concentration

$$a + 2y + z$$

From this must be deducted the osmotic pressure of the HCl of the outside aqueous solution. If x is the molar concentration of the H ions of the outside solution, it is also the molar concentration of the Cl ions. Hence the observed osmotic pressure of a protein solution is determined by the following molar concentration

$$a + 2y + z - 2x$$

Figure 7 shows how this value varies with the pH of the protein solution (*i.e.*, with y). In order to arrive at a theory concerning the influence of HCl on the osmotic pressure of protein solutions, it is necessary to calculate the osmotic pressure due to the value of $2y + z - 2x$ and to deduct it from the observed osmotic pressure of the protein solution. The osmotic pressure determined by the value $2y + z - 2x$ we will call the "Donnan correction." In this term, y and x can be calculated from the measurements of the pH, pH inside being $-\log y$ and pH outside

being $-\log x$. z can be calculated from x and y with the aid of the Donnan equation (1)

$$z = \frac{(x+y)(x-y)}{y}$$

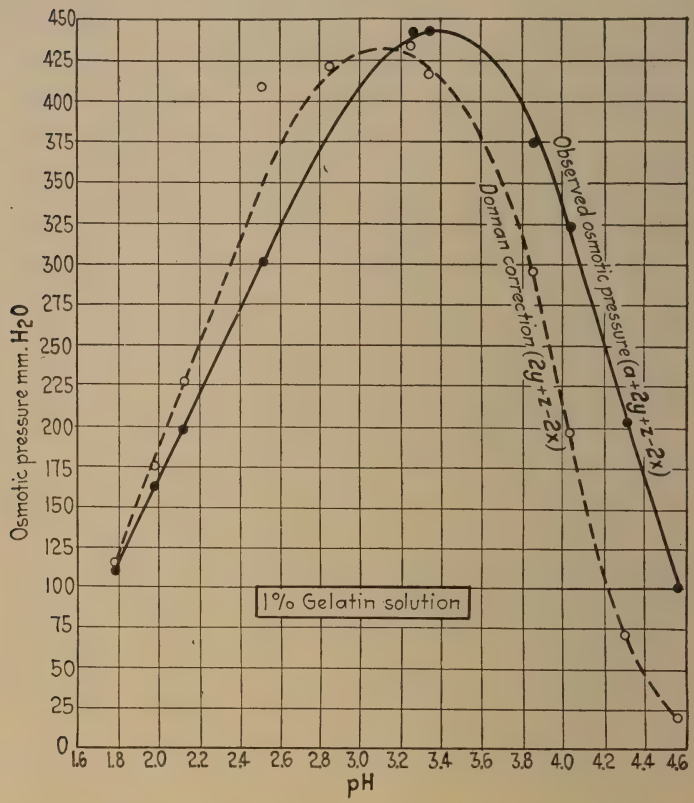

FIG. 9.—Showing agreement and minor discrepancies between the curves of observed and calculated osmotic pressures of 1 per cent gelatin chloride solutions.

since we now know through the experiments on membrane potentials that x and y are determined by the Donnan equilibrium. If the value of $2y + z - 2x$ is calculated for different pH of a gelatin chloride solution (of the same concentration of originally isoelectric gelatin, which in this case was 1 per cent); and if from this value is calculated the osmotic pressure due to this excess

of the molar concentration of crystalloidal ions inside the protein solution over that outside, on the basis of van't Hoff's theory of osmotic pressure, it is found that the curve for the Donnan correction is almost, but not quite, identical with the curve for the observed osmotic pressure (Fig. 9). In other words, it turns out that the increase in osmotic pressure of a 1 per cent solution of originally isoelectric gelatin upon the addition of little acid until a maximum is reached, and the diminution of osmotic pressure upon the addition of further acid, are not due to any variation in the state of dispersion of the protein, or any other real or imaginary "colloidal" property of the protein, but purely to the fact that protein ions cannot diffuse through the collodion membrane, which is easily permeable to crystalloidal ions. As a consequence, the molar concentration of the crystalloidal ions must always be greater inside the protein solution than outside. What varies with the pH of the gelatin solution is the value of $2y + z - 2x$. This follows from the Donnan equation (1), according to which

$$x = \sqrt{y^2 + yz} \text{ or } 2x = \sqrt{4y^2 + 4yz}$$

while

$$2y + z = \sqrt{4y^2 + 4yz + z^2}$$

Now, it is obvious that

$$\sqrt{4y^2 + 4yz + z^2} > \sqrt{4y^2 + 4yz}$$

i.e., the concentration of the crystalloidal ions inside the protein solution $2y + z$ is always greater than the concentration of the crystalloidal ions $2x$ outside, when z is not 0 or ∞.

If we substitute for the term $2y + z - 2x$ of the Donnan correction the identical term

$$\sqrt{4y^2 + 4yz + z^2} - \sqrt{4y^2 + 4yz}$$

we can visualize why the osmotic pressure is a minimum at the isoelectric point, why it increases with the addition of little acid, reaching a maximum, and why it diminishes again with the addition of more acid.[44]

At the isoelectric point no protein is ionized and, z being zero, the whole term

$$\sqrt{4y^2 + 4yz + z^2} - \sqrt{4y^2 + 4yz}$$

[44] Loeb, J.: *Science*, **56** (1922), 731.

becomes zero. Hence, at the isoelectric point the observed osmotic pressure is purely that due to the protein, which is very low on account of the high molecular weight of gelatin.

When little acid, *e.g.*, HCl, is added to the solution of isoelectric gelatin, gelatin chloride is formed and some free acid remains, due to hydrolytic dissociation. Hence both z (the concentration of Cl ions in combination with protein) and y (the Cl ions of the free HCl existing through hydrolysis) increase, but z increases at first more rapidly than y, and, hence, the excess of concentration of ions inside over that of ions outside increases until the greater part of protein is transformed into protein chloride, when the excess of crystalloidal ions inside over those outside reaches a maximum. From then on z increases comparatively little, while y increases considerably with further addition of acid, so that z becomes negligible in comparison with y. This explains why the Donnan correction becomes zero again when enough acid is added, and why the observed osmotic pressure becomes as low again as at the isoelectric point.

In the same way it can be shown why the addition of salt has only a depressing effect on the osmotic pressure. Let us assume that there is inside the bag a gelatin chloride solution of pH 3.0 to which NaCl is added. z (the concentration of Cl ions in combination with the gelatin) will not increase with the addition of salt, while y (the concentration of the Cl ions *not* in combination with gelatin) will increase. Hence, with the increase in the concentration of the salt the value of

$$\sqrt{4y^2 + 4yz + z^2} - \sqrt{4y^2 + 4yz}$$

will become smaller, finally approaching zero.

When another salt than a chloride, *e.g.*, $NaNO_3$, is added to a solution of gelatin chloride, we may assume that the gelatin in solution becomes gelatin nitrate.

Figure 9 gives a comparison of the curves for the observed osmotic pressure and for the osmotic pressure calculated from the Donnan correction. Both curves rise in a parallel way from the isoelectric point, reaching a maximum which is 450-mm. water pressure in the case of the observed osmotic pressure and slightly lower in the case of the Donnan correction. The observed osmotic pressure should be higher than the osmotic pressure

calculated from the Donnan correction by the osmotic pressure due to the protein molecules and ions. An almost constant difference exists in the two curves between pH 4.6 and 3.2, but disappears later, and this difference is in all probability the expression of the value of *a*, *i.e.*, the osmotic pressure due to the protein itself. The disappearance of this difference at pH below 3.2 is probably due to the fact that an error of one unit in the second decimal of the pH causes a considerable error in the calculations of *z*, which increases when the pH becomes smaller.

Figure 9 shows that when we correct the observed osmotic pressure for the Donnan effect it follows that the influence of the pH of the acid on the osmotic pressure is entirely or practically entirely due to the excess of the concentration of crystalloidal ions inside the membrane over that outside and that this excess is caused by the Donnan equilibrium. The osmotic pressure of the protein itself is either not altered at all by the addition of acid or, if it is altered, the effect is too small to be noticeable. There is then nothing left for the "dispersion theory" or for any other of the colloidal speculations to explain. This conclusion was confirmed by experiments on crystalline egg albumin and casein by the writer[45] and on edestin by Hitchcock.[46]

We can, therefore, summarize these results by stating that the so-called colloidal behavior of protein solutions, as far as membrane potentials and osmotic pressure are concerned, is merely the result of an equilibrium condition of classical chemistry, which results in an excess of the concentration of crystalloidal ions inside the protein solution over that of an outside aqueous solution, when the two solutions are separated by a membrane which is permeable to crystalloidal ions but impermeable to protein ions. The colloidal behavior of proteins depends, therefore, entirely on the relative non-diffusibility of protein ions through membranes which are easily permeable to crystalloidal ions. Since the majority of membranes in plants and animals belong to this class, it can easily be surmised how great a rôle the proteins must play in the regulation of osmotic pressure in the body and the distribution of electrolytes between the body liquids and the cells.

[45] Loeb, J.: *J. Am. Chem. Soc.*, **44** (1922), 1930.
[46] Hitchcock, D. I.: *J. Gen. Physiol.*, **4** (1921–22), 597.

Swelling.—Procter and Wilson[47] have shown that the influence of HCl on the swelling of gelatin is a purely osmotic effect. The acid, combining with the gelatin, causes salt formation, the gelatin ions being prevented from diffusing by the cohesive forces between the gelatin ions or molecules of the gel. Since the gel is freely permeable to water and crystalloidal ions, such as H and Cl, the non-diffusibility of the gelatin ions causes the establishment of a Donnan equilibrium between gelatin and outside solution, as a result of which the total molar concentration of all the diffusible crystalloidal ions is greater inside than outside the gel. This causes the influence of the acid on the swelling of gelatin and this influence is the same as that on osmotic pressure, for the reason that the influence of acid on swelling is also an osmotic pressure effect. The difference between the effect of acid on the osmotic pressure of gelatin solutions and on the swelling of gelatin gels is simply this—that in the former case the diffusion of the gelatin ions is blocked by the collodion membrane, and in the latter case by the cohesive forces between the gelatin molecules or gelatin ions of the gel.

These cohesive forces are also the limiting force to the swelling of a gel. Isoelectric gelatin absorbs a certain quantity of water, due to forces which have probably nothing to do with the Donnan equilibrium, since at the isoelectric point protein is only slightly ionized. The absorption of water by isoelectric gelatin is determined by forces of attraction between certain groups of the gelatin molecule and water, and is primarily, though perhaps not exclusively, a case of solid solution.[48] The additional swelling caused by the addition of acid is, however, as Procter and Wilson have shown, an osmotic phenomenon due to the excess in the concentration of H and Cl ions inside over that outside. This causes the diffusion of water into the gel. The hydrostatic pressure of the water will force the molecules of the gel apart and this will cause an increase in the forces of cohesion, which will

[47] Procter, H. R.: *J. Chem. Soc.*, **105** (1914), 313; Procter, H. R. and Wilson, J. A.: *J. Chem. Soc.*, **109** (1916), 307; Wilson, J. A. and Wilson, W. H.: *J. Am. Chem. Soc.*, **40** (1918), 886; Wilson, J. A.: *J. Am. Leather Chem. Assoc.*, **12** (1917), 108; "The Chemistry of Leather Manufacture," New York, 1923.

[48] Loeb, J.: "Proteins," p. 193.

oppose the further swelling. To give an idea of the difference between the swelling of isoelectric gelatin and that due to the influence of acid, it may be stated that while 1 g., dry weight, of powdered isoelectric gelatin absorbed about 7 g. of water, the same gelatin, when under the influence of an acid with monobasic anion, absorbed about 35 g. of water at pH 3.2 or 3.0 (of the gel), where the swelling is a maximum.[49] The forces of cohesion between the molecules or ions of the gel may be modified by the solute, *e.g.*, the anion of the acid, and when this happens, the pure osmotic pressure effect, due to the Donnan equilibrium, may not be observed. This was noticed in the effect of acids on the swelling of casein, where it was found that swelling occurs in HCl or HNO_3, but not in trichloroacetic acid.[50] These secondary effects of the anion of the acid or of the undissociated acid on the cohesion of the gel are slight and negligible in the case of a gel of gelatin, and, for this reason, the validity of the valency rule can easily be demonstrated for the influence of acids on the swelling of gelatin.

The method of calculating the effect of HCl on the swelling of the gel from the Donnan equilibrium is similar to that for calculating the osmotic pressure, but is complicated by the necessity of introducing the cohesive forces of the jelly. Since space forbids to go into the derivation of the equation of Procter and Wilson, the reader is referred to their original papers or to Wilson's[51] or the writer's book.[52] Chapters I and XXX of this treatise by Wilson and Procter respectively develop this point. Figures 1 and 2 of Chapter I (pages 17—18) show the excellent agreement between Procter's and Wilson's values calculated on the basis of Donnan's theory of membrane equilibria and the observed values for swelling.

If the influence of acid on the swelling of gelatin is due to the Donnan equilibrium, the influence of different acids on swelling must depend solely on the valency but not the nature of the anion

[49] Loeb, J. and Kunitz, M.: *J. Gen. Physiol.*, **5** (1922–23), 665.

[50] Loeb, J. and Loeb, R. F.: *J. Gen. Physiol.*, **4** (1921–22), 487; Loeb, J.: "Proteins," p. 193.

[51] Wilson, J. A.: "The Chemistry of Leather Manufacture," New York, 1923.

[52] Loeb, J.: "Proteins," p. 190.

of the acid. Figure 10 gives the results with different acids. The abscissæ are the pH of the gel at the end of the experiment, while the ordinates are the weight of the gelatin at the end of the experiment. All the values for the influence of the six monobasic acids, HCl, HBr, HI, HNO_3, propionic, and lactic acid, on swelling lie on the same curve within the limits of the accuracy of the experiments, with a maximal weight of about 36 g., which is inside the variations for the controls with HCl referred to. Only acetic acid gives a slightly higher maximal value of about

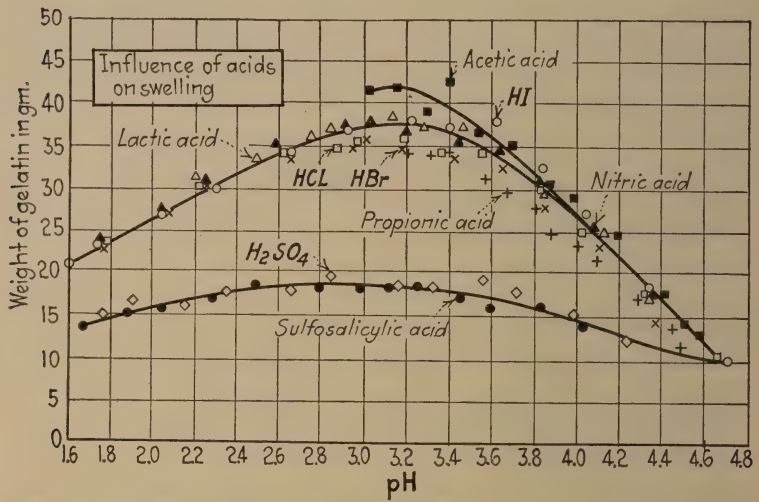

Fig. 10.—Proof of valency rule for the influence of acids on the swelling of gels of gelatin. The influence of the seven monobasic acids is (aside from slight secondary effects of acids presumably on the cohesion of the gel) the same and considerably higher than that of the two dibasic acids.

42 g. at pH 3.2. The abnormal behavior of acetic acid does not occur in either membrane potentials or osmotic pressure, where the effects are due to isolated gelatin ions. The suspicion is, therefore, justified that the excessive effect of acetic acid on swelling is due to a diminution of the cohesion of the gel caused by the high concentration of acetic acid required to bring the pH to 3.2 or 3.0.[53]

On the other hand, the strong dibasic acids, H_2SO_4 and sulfosalicylic acid, also act alike but cause a maximal weight of only

[53] Loeb, J. and Kunitz, M.: *Loc. cit.*

18 g., which is about one-half of the maximal weight of the gelatin under the influence of HCl. This ratio of 1:2 for dibasic and monobasic acids is about the same as that observed for the valency effect of anions in the case of osmotic pressure. The maximum lies at a pH of about 3.0 to 3.2 of the gel.

Figure 11 shows the effect of weak dibasic and tribasic acids on swelling. From what has been said concerning the electrolytic dissociation of these acids it is obvious that their effect on swelling is also as clearly a confirmation of the valency rule as is their action on membrane potentials and on osmotic pressure. Such

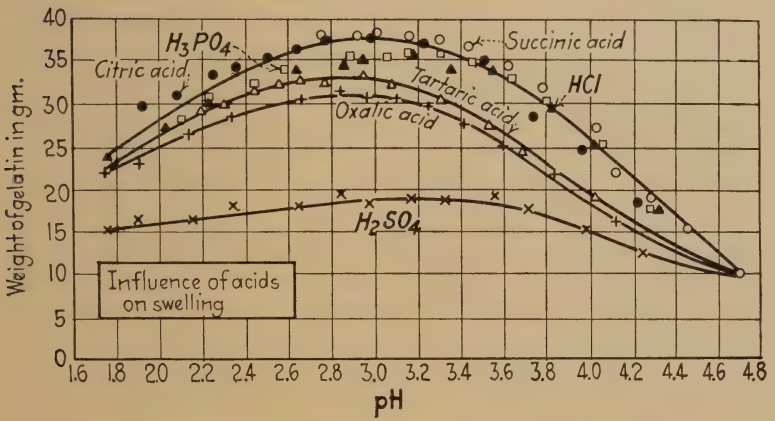

Fig. 11.—Influence of weak dibasic and tribasic acids on swelling.

an influence of valency without influence on the chemical nature of the anion of an acid occurs only in properties which depend upon the Donnan equilibrium. The fact that the influence of acid on swelling is an osmotic effect explains why the curves representing this influence are similar to the curves representing the influence of acids on osmotic pressure.

Viscosity.—It may seem strange that the influence of electrolytes on the viscosity of certain protein solutions should be explained in the same way, but this seems to be the case. There are two types of viscosity, one type which holds for all kinds of solutions and one type which is specifically colloidal. We are concerned only with the latter type of viscosity, which is of a comparatively high order of magnitude. According to Einstein's

formula, the viscosity of an aqueous protein solution is a linear function of the relative volume of the solute occupied in the solution, as expressed in the equation

$$\eta = \eta_o(1 + 2.5\varphi)$$

where η is the viscosity of the solution, η_o that of pure water, and φ the ratio of the volume of the solute to that of the solution. If, therefore, the addition of little acid to a 1 per cent solution of isoelectric gelatin increases the viscosity of the solution until a maximum is reached, and if the addition of more acid depresses the viscosity again, it follows that the addition of acid changes the relative volume occupied by the gelatin in water. This is only possible by water being absorbed by the protein and the question is how to account for this absorption of water by the protein under the influence of acid. Pauli assumed that the ionized protein surrounds itself with a jacket of water, which is lacking in the non-ionized protein. If this were true, all the proteins and amino acids should show a similar influence of acid on the viscosity of their solutions. The writer found that no such influence exists in the case of amino acids and at least one protein, namely, crystalline egg albumin. If Pauli's assumption were correct, there is no reason why crystalline egg albumin should not show an influence of acid on viscosity of the same order as that which is found in the case of gelatin. The difference between gelatin and crystalline egg albumin is that the former sets to a solid gel if the temperature is not too high, while the latter does not. The formation of a continuous gel in the gelatin solution is preceded by the formation of submicroscopic aggregates which occlude water and which are capable of swelling, and these aggregates or precursors of the continuous gel increase in size and number on standing. To test this idea the writer made experiments with suspensions of powdered gelatin in water and found that such suspensions of powdered gelatin had a much higher viscosity than a freshly prepared solution of gelatin containing the same quantity of gelatin. This was to be expected, if the influence of acid on the viscosity of proteins is due to the swelling of submicroscopic particles of gel. It harmonizes with this fact that the viscosity of solutions of crystalline egg albumin is of a low order of magnitude, which was to be expected if solu-

tions of crystalline egg albumin contain few or no micelles. It was found, moreover, that the viscosity of suspensions of powdered gelatin increased under the influence of acid or alkali in the same way as did the swelling of jellies or the osmotic pressure of gelatin solutions. The viscosities were measured at 20°C. When the suspension of powdered gelatin was melted, it was found upon rapid cooling to 20°C. that the viscosity was considerably lower and that the influence of acid had almost disappeared. By these and a number of similar experiments it was possible to prove that the similarity between the influence of electrolytes on the viscosity of gelatin solution and the influence of electrolytes on osmotic pressure is due to the fact that the influence on viscosity in such cases is in reality an influence on the swelling of submicroscopic protein particles, *i.e.*, a function of osmotic pressure. This proof was made complete by showing that there exists a Donnan equilibrium between powdered particles of gelatin and a surrounding weak gelatin solution. The reader is referred to the writer's book and papers for further details.[54]

The Action of Salts.—A few words must suffice to explain the action of salts on the four colloidal properties of proteins. Salts do not raise the value of z but only of y in equations (1) and (2), and, as a consequence, salts can only diminish the excess in the concentration of the diffusible ions inside the protein solution or protein gel over that outside. This explains the purely depressing effect of salts on the values of the four colloidal properties. It follows, furthermore, that only the anion of a salt should be able to influence the four colloidal properties of protein chloride; namely, membrane potentials, osmotic pressure, swelling, and that type of viscosity which depends on the swelling of submicroscopic particles of proteins. Furthermore, it follows that the valency only but not the chemical nature of the ions of a salt should have such a depressing effect. The limited space permits us only to show that this is true for the action of salts on osmotic pressure and swelling.

In such experiments it is necessary to guard against the possibility of any change in the pH by the addition of the salt to the protein solution or the protein gel. The methods of avoiding this error are given in the writer's book and more explicitly

[54] LOEB, J.: "Proteins," p. 150.

in a recent paper.[55] Earlier workers had failed to measure the hydrogen ion concentration of their protein solutions and gels and to compare the effects of salts at the same pH of the protein solution or gel, and, hence, mistook the effect of variations of the pH (which they overlooked) for effects of the anion of the acid added. This gave rise to the myth of the so-called Hofmeister ion series in colloidal behavior, according to which not only the valency but also the chemical nature of the ions of a salt are said to have an effect on the colloidal behavior of proteins. This statement is altogether incorrect insofar as it applies to those properties of proteins which depend on the Donnan equilibrium, such as membrane potentials, osmotic pressure, swelling, and that type of viscosity which is due to the swelling of submicroscopic particles, since these properties are affected only by the valency and not by the chemical nature of the ion. Crystalloidal properties of proteins, however, such as solubility, cohesion, diffusion potentials, etc., depend, of course, not only on the valency but also on the chemical nature of the ions of a salt. As long as the colloid chemists will continue in their failure to measure and to consider the pH of their solutions, and as long as they will continue to struggle against the acknowledgment of the fact that the Donnan equilibrium is the basis of the strictly colloidal behavior (at least as far as the proteins are concerned), so long will they fail to understand that the Hofmeister ion series (for the four colloidal properties of proteins) are not only experimental errors but theoretically impossible. They will also fail to understand that the chemical nature of the ions of a salt must play a rôle in crystalloidal behavior while it cannot play a rôle in the colloidal properties which depend on the Donnan equilibrium.

Figure 12 gives the influence of seven salts, NaCl, NaBr, $NaNO_3$, NaI, NaCNS, Na acetate, and Na_2SO_4, on the osmotic pressure of a solution of gelatin chloride of pH 3.8, special care being taken that the pH was not altered by the addition of salt, through measurements of the pH with the hydrogen electrode.[56] The depressing effects of the six salts with monovalent anion

[55] Loeb, J.: "Proteins," p. 99; Loeb, J. and Kunitz, M.: *J. Gen. Physiol.*, **5** (1922–23), 693.

[56] Loeb, J. and Kunitz, M.: *J. Gen. Physiol.*, **5** (1922–23), 701.

(NaCl, NaBr, NaI, $NaNO_3$, NaCNS, Na acetate) on the osmotic pressure of the gelatin chloride solutions of pH 3.8 (containing 1 g. dry weight of originally isoelectric gelatin in 100 cc.) lie, within the limits of experimental accuracy, on one curve, which is entirely

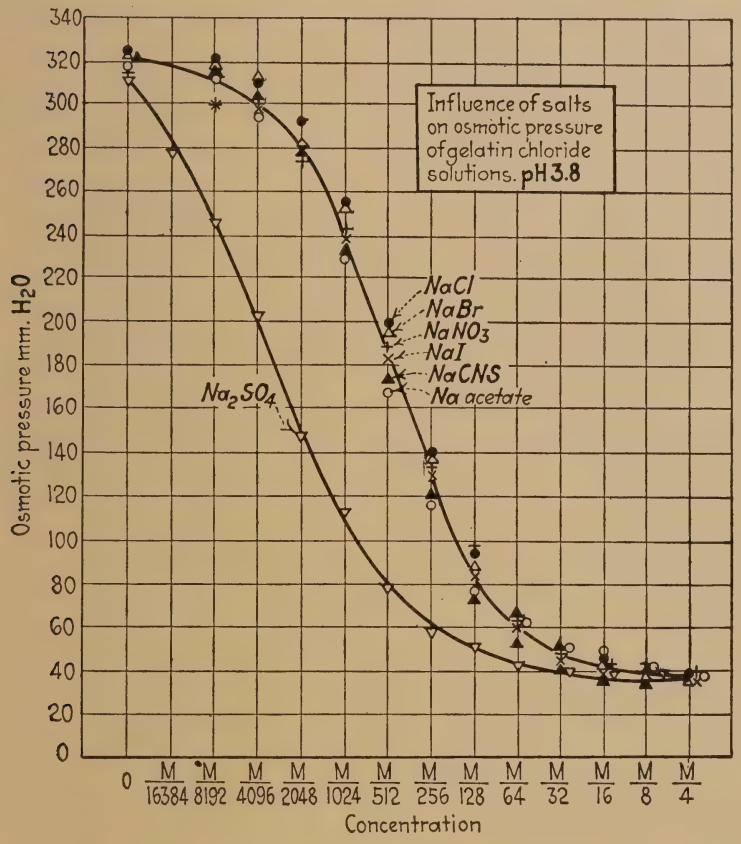

FIG. 12.—All salts with monovalent anions depress the osmotic pressure of gelatin chloride solutions of pH 3.8 to the same extent (within the limits of experimental accuracy). Na_2SO_4 depresses considerably more.

different from the curve for the effect of Na_2SO_4. The osmotic pressures are a little over twice as high when the anion of the salt is monovalent than when it is divalent. The variations in the effects of the six salts with monovalent anion are chance varia-

tions, since they are also found when no salt is added, *i.e.*, at concentration 0 in Fig. 12.

This shows that all the salts with monovalent anions have the same effect on the osmotic pressure when the pH is kept constant and that the so-called Hofmeister anion series is based on error. The anion series must be replaced by the valency rule. This statement is supported by experiments on the influence of Na_2 oxalate, Na_2 tartrate, and Na_2 succinate upon the omostic pressure. The effect of these salts lies between that of Na_2SO_4 and NaCl as the valency rule demands.

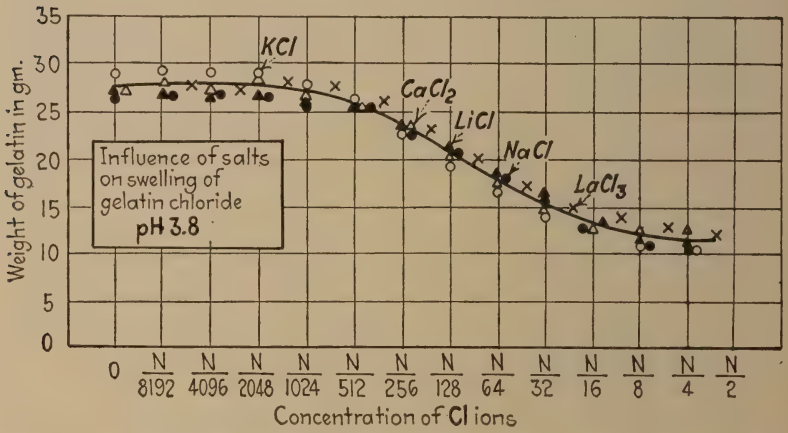

FIG. 13.—All chlorides depress the swelling of a gelatin chloride gel of pH 3.8 to the same extent at the same concentration of Cl ions.

Figure 13 gives the influence of five chlorides, KCl, NaCl, LiCl, $CaCl_2$, $LaCl_3$, on the swelling (measured by weight of the gel) of a gel of gelatin chloride containing 1 g., dry weight, of originally isoelectric gelatin. The pH of the gel at equilibrium was 3.8. The abscissæ are the concentrations of the Cl ions of the salts and the ordinates the weight of the gel. It is obvious that all five salts depress the swelling equally at the same concentration of Cl and that, hence, the cation of the salt has no effect.

The next fact to be ascertained was whether or not only the valency of the anion of the salt is of influence or whether the anion series generally quoted in colloidal literature is valid, according to which the swelling is a maximum in NaCNS, and a

minimum in Na acetate (leaving the divalent anions out of consideration for the present).

Seven salts with monovalent anions were tried, namely, NaCl, NaBr, NaI, $NaNO_3$, NaCNS, Na acetate, and Na lactate. The

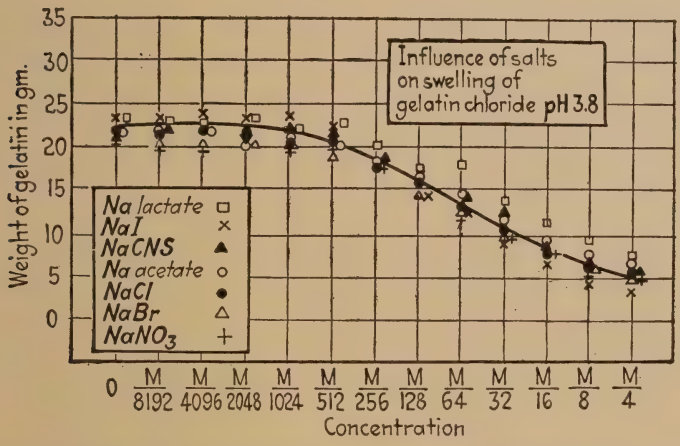

FIG. 14.—All salts with monovalent anions depress the swelling of a gelatin chloride gel to the same extent (within the limits of experimental accuracy) at pH 3.8.

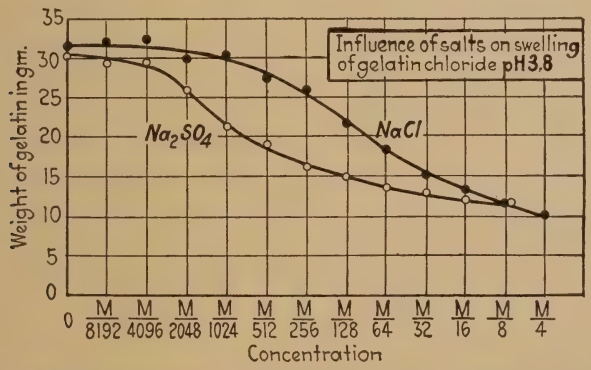

FIG. 15.—Na_2SO_4 depresses the swelling of a gelatin chloride gel considerably more than NaCl.

results are given in Fig. 14. It is obvious that the effects of all of these seven salts lie on one curve, and that the variations are essentially the chance variations due to the limits of experimental accuracy. This is proved by the fact that the same variations

are observed when the concentration of salt is zero, *i.e.*, when no salt is added. There is not the slightest indication of the Hofmeister anion series. Slight influences of the salts on the cohesion of the gel of gelatin may exist, but they are too small to play a rôle.

While salts with monovalent anions have the same depressing effect for the same concentration of anions, salts with bivalent anions have a much greater depressing effect on swelling than salts with monovalent anions. This is illustrated in Fig. 15, showing the difference in the effect of equal molar concentrations of NaCl and Na_2SO_4 on swelling. NaCl does not depress swelling in concentrations of $\frac{M}{1,024}$ or below, and the depressing effect of NaCl on the swelling of gelatin chloride of pH 3.8 commences to be noticeable at a concentration of $\frac{M}{512}$. This is true for all salts with monovalent anions, as Fig. 14 shows. Na_2SO_4 begins, however, to depress at a concentration between $\frac{M}{4,000}$ and $\frac{M}{2,000}$, and the curve for the SO_4 effect drops much more rapidly to the minimum than in the case of NaCl. Since, however, the degree of swelling of a gel does not only depend on the osmotic pressure of the solution inside the particle but also upon the force of cohesion, and since the cohesion may also be influenced by the electrolytes added, it is necessary to guard against a confusion of the two possible effects of an electrolyte. These effects on cohesion are especially noticeable in high concentrations of electrolytes. The cohesion effect of electrolytes has nothing to do with the Donnan equilibrium and, hence, in such cases an influence of the chemical nature of the efficient ion may be observed. Such cohesion effects may appear especially in higher concentrations of electrolytes and this explains some of the statements in colloid literature.

Summarizing all the results, we can say that the membrane potentials, osmotic pressure of gelatin chloride solutions, or the swelling of gelatin chloride gels, and that type of viscosity of gelatin chloride solutions which depends on the swelling of submicroscopic solid particles in the solutions are affected only

by the anion but not by the cation of a salt; that all anions of the same valency have the same depressing effect on these four properties of gelatin chloride, and that the depressing effect is greater for the divalent than for monovalent anions. Such a result is possible only for properties depending on the Donnan equilibrium.

The total result of these investigations is that it is incorrect to distinguish between colloids and crystalloids—at least as far as the proteins are concerned—but that we must distinguish instead between colloidal and crystalloidal properties. Proteins are crystalloids, both in regard to their chemical reactions and their solubility, but on account of the large size of their ions they easily fulfill the condition for the establishment of a Donnan equilibrium, namely, that the protein ion is prevented from diffusing through membranes or gels which are easily permeable to the smaller crystalloidal ions. Those properties of the proteins which depend on the Donnan equilibrium constitute their colloidal behavior. For the sake of convenience, we may continue to distinguish between colloids and crystalloids, but in that sense only that colloids possess large ions, the diffusion of which is blocked by dialyzing membranes permeable to the smaller ions of typical crystalloids. There is, however, no further justification for any distinction between the chemistry or solubility of colloids and of crystalloids, as far as the proteins are concerned. That the rôle of the Donnan equilibrium for the colloidal behavior of proteins had been overlooked was again due to the fact that the majority of the workers in this field never measured the hydrogen ion concentration of their protein solutions or gels. Without such measurements it was impossible to notice the rôle which the Donnan equilibrium plays in these phenomena.

CHAPTER III

THE FLOCCULATION AND STABILITY OF COLLOIDAL SUSPENSIONS

By

JOHN H. NORTHROP

One of the most striking characteristics of suspensions of finely divided matter is the fact that under certain conditions the individual particles remain discrete, whereas under other conditions they collect into larger aggregates. Under the former conditions the rate of settling is very slow and the suspension may be returned to its original condition by mechanical disturbances, whereas under the latter the particles settle rapidly and, in general, cannot be made to separate and return to their original state. This peculiarity of such systems is of great theoretical and practical interest and has been the subject of a very large number of papers. It is the fundamental phenomenon concerned in the formation of deltas by the sedimentation of river silt in the ocean, of the production and use of colloidal fuels and emulsions, the agglutination of bacteria, and innumerable other common processes. It is impossible in so short a space as can be devoted to this chapter more than to outline the clearest cut results. General reviews covering the entire field may be found in the books of Freundlich,[1] Burton,[2] Bancroft,[3] and Taylor.[4]

A suspension undergoing the process of flocculation presents a definite series of changes. At first the individual particles cannot be seen except with the microscope. Their presence is shown, however, by a Tyndall cone when light is passed through the suspension. Larger particles then make their appearance and

[1] FREUNDLICH, H.: "Kapillarchemie," 2nd ed., Leipzig, 1922.

[2] BURTON, E. F.: "The Physical Properties of Colloidal Solutions," 2nd ed., London, New York, Bombay, Calcutta, and Madras, 1921.

[3] BANCROFT, W. D.: "Applied Colloid Chemistry," New York and London, 1921.

[4] TAYLOR, W. W.: "Chemistry of Colloids," 3rd ed., New York, 1915.

may usually be seen as discrete clumps. These clumps consist, in general, of a number of small particles adhering firmly together but still retaining their individual form. More or less rapid settling of these larger particles now occurs and in the course of time the solid matter forms a precipitate on the bottom of the vessel, leaving a clear liquid above. The suspension is now flocculated or "sedimented." The appearance under the microscope is similar, except that, in addition, it can be seen that the small particles are in rapid irregular movement—the Brownian movement—whereas the large clumps are stationary. It can also be usually seen that the particles do not actually coalesce but merely approach one another closely. (In the case of the "breaking" of an emulsion there is actual coalescence; this is a distinct phenomenon and will not be considered here.)

It may be seen from the above brief description that the phenomenon can be divided into two distinct steps: first, the collection of the small particles into larger aggregates, and, second, the settling of these aggregates to the bottom of the vessel. In regard to the latter effect, the small and large particles differ from each other both in the rate of settling and in the final condition of equilibrium, although under ordinary conditions the difference in the rate is of the greater significance.

Effect of the Size of Particles on the Rate of Settling

The formula for the steady rate of fall of a small body in a viscous medium was given by Stokes as

$$V = \frac{\frac{2}{9}a^2 (D - d)\, g}{z} \qquad (1)$$

where a is the radius, D the density of the particle, d the density of the solution, z the viscosity of the solution, and g the acceleration due to gravity. This formula was tested by Perrin[5] for small particles by comparing the radius calculated from the rate of fall with that determined by direct measurement or calculated from the weight and size.

Radius in μ Determined by		
Direct Measurement	Weighing	From Stokes' Law
0.371	0.3667	0.3675

[5] Perrin, J.: "Die Atome," Dresden, 1914, p. 90.

The experiment shows that the particles obey Stokes' law with the greatest exactness. This result is of special importance, since the validity of Stokes' law is assumed in all calculations concerning the Brownian movement. It follows, therefore, that the speed of settling of different size particles, other conditions being the same, will increase with the square of the radius and the difference in rate between visible and microscopic particles will be enormous. In Perrin's experiments the rate was a few millimeters a day.

Effect of the Size of Particles on the Final Equilibrium

The English botanist, Brown, noted that pollen grains as seen under the microscope possessed rapid irregular movements. This peculiar constant motion has become known as the Brownian movement. It was soon found that the motion was independent of the nature of the particles and could not be ascribed to any outside influence. It is less in viscous liquids and very rapid in gases. The motion is less in large particles. It follows from the doctrine of equipartition of energy that the mean kinetic energy ($\frac{1}{2}\ mv.^2$) of the particles must remain constant. The velocity decreases rapidly, therefore, as the size increases.[6] Svedberg has shown that it is not affected by the potential of the particle nor by the addition of electrolytes.[7] It was suggested by Wiener that this motion was due to the bombardment of the particles by the molecules of the solvent. The motion, therefore, becomes strictly analogous to the kinetic motion of the molecules themselves. A quantitative theory for this motion was worked out independently by Einstein and by v. Smoluchowski and verified experimentally by Perrin. The part of the theory which is of interest in this connection is the prediction regarding the final distribution of the particles at equilibrium. If the Brownian movement is really analogous to the kinetic motion of gases, then the distribution of the particles at equilibrium should be determined by the same law that regulates the density of a gas at

[6] Lewis, W. C. McC.: "A System of Physical Chemistry," London, New York, Bombay, Calcutta, and Madras, 1920, vol. 1, chap. I.

[7] For a thorough discussion of the Brownian movement, see Burton, E. F.: "The Physical Properties of Colloidal Solutions," p. 50; Perrin, J.: "Die Atome," Dresden, 1914, p. 83; Freundlich, H.: "Kapillarchemie," 2nd ed., Leipzig, 1922, p. 469.

different levels. Equilibrium will be established when the effect of gravity exactly equals the osmotic pressure (in this case the Brownian movement) of the particles or molecules. In the case of gases this formula is

$$h = \frac{RT}{gM} \ln \frac{p_o}{p}$$

where h is the height, p_o the pressure at the bottom of the column, p the pressure at height h, g the acceleration due to gravity, and M the molecular weight.[8] Since the osmotic pressure is proportional to the number of particles per unit of volume, the formula, as applied by Perrin to suspensions, becomes

$$h = \frac{RT}{gN\frac{4}{3}\pi r^3(D - d)} \ln \frac{n_o}{n} \qquad (2)$$

in which N is Avogadro's number, D is the density of the particle, and d the density of the liquid.

The formula shows that the height necessary to give any relative pressure compared to the pressure at the bottom varies inversely as the weight of the particles. If the weights of the particles are as 100,000,000 to 1, then the height at which the pressure will be half that of the bottom pressure will be in the same ratio, *i.e.*, if a particle 100,000,000 times as heavy as an oxygen molecule is compared to oxygen, the height at which the pressures (or concentration of particles) is halved will be as 50μ to 5,000 meters.[9] The formula was tested by Perrin by measuring the concentration of particles at various heights and determining the diameter and density of the particles as well as the density of the liquid.

He found[10] that the concentration of particles decreased in geometric proportion as the height increased in arithmetic proportion, as the following figures show.

Height in μ	Relative Number of Particles
5	100.0
35	47.0
65	22.6
95	12.0

[8] Freundlich, H.: "Kapillarchemie," 2nd ed., Leipzig, 1922, p. 469.
[9] Perrin, J.: "Die Atome," Dresden, 1914, p. 94.
[10] *Ibid.*, p. 95.

This is the relation predicted. It follows that at equilibrium the number of particles of microscopic size at any appreciable height from the bottom would be very small.

The critical test of the theory, however, was the calculation of Avogadro's number N. The accepted value for this constant from measurements with gases is 61×10^{22}, whereas Perrin found 68×10^{22}. The agreement is astounding when it is remembered that the measurements were made on particles approximately 100,000,000 times the mass of gas molecules.

Perrin's experiments leave little doubt that the relation between the size of the particles, the rate of settling and the final distribution is accurately expressed by formulas (1) and (2). If the necessary data regarding the size of the particles, the viscosity of the solution, etc., are known, it is, therefore, possible to calculate both the rate of fall of the particles and the final state of equilibrium. Briefly, it may be said that if the size alone is varied, the rate at which the particles fall will increase as the square of the radius and that at equilibrium the distance from the bottom, at which the concentration of particles will be halved, will be inversely proportional to the mass. The difference in the behavior of suspensions before and after the formation of larger aggregates is, therefore, clearly accounted for, and it only remains to determine what forces or conditions regulate the formation of agglomerations of particles.

If a stable suspension is observed under the microscope, it may be seen that, although the particles approach each other, they do not actually collide. If some substance is now added which precipitates the suspension, the particles then collide and stick together. Since they sometimes adhere to each other and sometimes remain separate, there must evidently be a force which tends to keep them apart and another force which holds them together. If the repulsive force is greater than the cohesive force, or greater than the momentum of the particles due to their movement, the particles will remain separate, whereas if it is less they will adhere into larger aggregates.

It has long been known that particles or surfaces in contact with liquids are electrically charged, since under the influence of an external e.m.f. the particles move. If the liquid moves while the solid is kept stationary, the phenomenon is known as electro-

endosmosis, whereas if the particles move through the liquid, it is known as cataphoresis.[11] It was early suggested that it was this repulsion, due to the charge carried by the particles, which prevented their touching each other, and practically all theories of the stability of suspension depend in some way on this potential difference between the particles and the surrounding liquid. In order to trace the connection between this property and the behavior of the particles, it is necessary to touch somewhat on the nature and origin of this potential difference.

Method of Measurement and Probable Nature and Origin of the Charges of Colloidal Suspensions

All methods of measurement of the charges carried by colloidal suspensions depend on determining the motion of the particles in an external field. This may be done either by noting the movement of the boundary of the suspension as a whole in a U-tube,[12] or by following the motion of a single particle under the microscope or ultramicroscope. (A convenient type of apparatus for these measurements has been described by the writer.)[13]

The potential between the surface of the particle and the surrounding film of liquid may then be calculated by the Lamb-Helmholtz formula.

$$\text{P.D.} = \frac{4\eta v \pi}{KX}$$

in which η is the viscosity, K the dielectric constant of the surface layer, v the velocity in centimeters per second, and X the potential gradient. All electrical units are electrostatic. Substituting the viscosity of water and the dielectric constant at 20°C. and changing to millivolts, the formula becomes

$$\text{P.D. in millivolts} = 13 \frac{\mu \text{ per second}}{\text{Volts per centimeter}}$$

This formula was derived on the assumption that each particle

[11] *Cf.* Freundlich, H.: "Kapillarchemie," 2nd ed., Leipzig, 1922, p. 326; Burton, E. F.: "The Physical Properties of Colloidal Solutions," 2nd ed., 1921, p. 125.

[12] Burton, E. F.: "The Physical Properties of Colloidal Solutions," 2nd ed., p. 131.

[13] Northrop, J. H.: *J. Gen. Physiol.*, **4** (1921–22), 629; Northrop, J. H. and Cullen, G. E.: *J. Gen. Physiol.*, **4** (1921–22), 635.

acts like a small condenser and is surrounded by a Helmholtz double layer. The charge on the particle as a whole, including the film of liquid, is, therefore, 0. A potential difference exists, however, between the two oppositely charged layers and it is between these layers that the motion occurs. It follows that the value for the dielectric constant of the liquid between the two layers should be inserted in the formula. There is no way of determining this value, however, so that the dielectric constant of the pure liquid is usually used. It has been found by numerous investigators that this formula is experimentally correct so far as it concerns the relation between the rate of migration and the impressed e.m.f., or the viscosity.[14] There is, however, no evidence concerning the correctness of the actual value of the potential calculated from the velocity. It was shown by Hardy that the size of the particles was without effect on the observed motion, which also agrees with the theory.

The theory of Helmholtz and Lamb gives us no information as regards the origin of this potential difference and no satisfactory theory has been suggested up to the present. It has been shown by Haber and Klemensiewicz,[15] that the cataphoretic potential is not the same as the Nernst electrode potential. This has been ascribed by v. Smoluchowski to the fact that the P.D. between the interior of the particle and the liquid is the Nernst potential, whereas the cataphoretic P.D. is between the movable and fixed films.

McTaggart's experiments with air bubbles and Lenard's measurements of waterfall electricity indicate that the source of the potential may be entirely in the film of liquid surrounding the particle.[16]

Wilson,[17] on the other hand, suggested that the P.D. was due to a Donnan equilibrium, and Loeb[18] has found that there is some analogy between the two but that quantitatively they are different. This theory accounts satisfactorily for the observation

[14] BURTON, E. F.: "The Physical Properties of Colloidal Solutions," 2nd ed., p. 137.

[15] FREUNDLICH, H.: "Kapillarchemie," 2nd ed., Leipzig, 1922, p. 341.

[16] *Cf.* LOEB, J.: *J. Gen. Physiol.*, **5** (1922–23), 515.

[17] WILSON, J. A.: *J. Am. Chem. Soc.*, **38** (1916), 1982.

[18] LOEB, J.: *J. Gen. Physiol.*, **5** (1922–23), 515.

that the sign of charge changes at the isoelectric point of the particle when the latter is amphoteric and accounts also for the relation between the ionization and the sign of charge. It is known, for instance, that substances which tend to dissociate as acids are usually negative and basic substances positive.

v. Hevesy[19] considers the particles as analogous to large ions. It is true that the rate of migration is about the same. There would seem to be a definite difference, however, between the mechanism by which the solution as a whole is kept electrically neutral. In the case of an ion there is always an equal number of ions of the opposite charge in the solution, whereas, according to the Lamb-Helmholtz theory, each particle as a whole is electrically neutral. In any case, it is certain that the P.D. of the particles is closely connected with the presence of electrolytes in the solution. It has been found by numerous workers that the more carefully the solution was freed from electrolytes the lower the potential and the more unstable the suspension.[20]

The general opinion at present appears to be that the charge is conferred by the combination of the particle with an ion, although the nature of this combination is uncertain.

Whatever the source of the potential on the particles, it follows that similarly charged particles would tend to repel each other and thereby render the suspension stable. If, however, the particle as a whole is electrically neutral, this repulsion would not obey Coulomb's inverse square law, but would only become effective when the particles approached each other so closely that the outside of the double layers overlapped. This conclusion is borne out by Perrin's observation[21] that the distribution of charged particles is abnormal when the distance between them is less than about 1.7 times the radius. When the charge is removed, this anomalous distribution disappears. This experiment furnishes strong evidence that the particles are held apart by their electric charge.

It was first noted by Hardy[22] that suspensions of denatured proteins were most unstable at the isoelectric point, and he sug-

[19] v. HEVESY, G: *Kolloid-Z.*, **21** (1917), 129.
[20] BEANS, H. T. and EASTLACK, H. E: *J. Am. Chem Soc.*, **37** (1915), 2667.
[21] PERRIN, J.: *Compt. rend.*, **158** (1914), 1168.
[22] HARDY, W. B.: *Proc. Roy. Soc.*, **66** (1900), 110.

gested that this was due to the fact that they were electrically neutral at this point. This conclusion was verified qualitatively by a large number of workers.[23] A number of cases were found, however, in which there seemed to be no direct connection between the stability and the potential.

Ellis[24] made a number of measurements on oil emulsions and found that the stability was closely connected with the potential. The experiments were then carefully carried out by Powis,[25] who made accurate measurements of the P.D. between the oil drops and surrounding liquid in a series of electrolyte solutions and found that whenever the potential between the drops and the surrounding liquid was reduced below about 30 millivolts, the particles collected into larger aggregates. A summary of Powis' results is given in Table I. They leave little doubt that in this case the potential is the decisive factor. It will be noted, however, that it becomes necessary to assume a critical P.D. instead of Hardy's zero potential. Powis found later that in the case of arsenic sulfide suspensions this critical P.D. was different for different salts. (This effect will be discussed below in connection with work on bacterial agglutinations.) A number of experiments were carried out by the writer on suspensions of typhoid bacteria. It was found that when these had been treated with an excess of antiserum they behaved in the same way as Powis' oil drops, *i.e.*, agglutination always occurred whenever the potential was reduced below a critical value of about 15 millivolts. A summary of these experiments is shown in Fig. 1.

A similar series of experiments was carried out by Loeb[26] on suspensions of collodion particles. The results are summarized in Table II. Here again there is no doubt that agglutination occurs whenever the P.D. is reduced below about 15 millivolts. The same result was obtained when the particles were previously treated with egg albumin, and with particles of denatured egg albumin.[27] These experiments leave little doubt that in these cases the potential is the determining factor for the stability of

[23] BURTON, E. F.: "The Physical Properties of Colloidal Solutions" 2nd ed., 1921, p. 149.

[24] ELLIS, R.: *Z. physik. Chem.*, **78** (1911–12), 321; **80** (1912), 597.

[25] POWIS, F.: *Z. physik. Chem.*, **89** (1914–15), 91, 179, 186.

[26] LOEB, J.: *J. Gen. Physiol.*, **5** (1922–23), 123.

[27] *Ibid.*: 485.

FIG. 1.—Effect of various electrolytes on the agglutination of typhoid bacteria sensitized with immune serum; — complete agglutination; — — — partial or no agglutination.

TABLE I[28]

Concentration, millimol/liter	Salt							
	KCl		$BaCl_2$		$AlCl_3$		$ThCl_4$	
	Oil-H_2O potential, mv.	Relative stability	P.D., mv.	Stability	P.D., mv.	Stability	P.D., mv.	Stability
	−46	1.00	−46	1.00	−46.0	1.00	−46.0	1.0
0.005	....	....	....	....	.....	1.00	−39.0	1.0
0.010	....	....	....	....	−38.0	0.80	− 6.5	0.3
0.020	....	....	....	....	.....	0.35	− 8.5	0.2
0.050	....	....	....	....	−17.0	0.35	+29.0	1.0
0.100	....	....	....	....	.....	....	.....	1.0
0.200	−50	1.00	−43	1.00	− 8.0	0.30	.....	1.0
0.500	....	....	....	....	.....	....	+52.0	1.0
1.000	−59	1.00	−30	0.75	+ 2.5	0.30		
2.500	−61	1.00	−25	0.45				
5.000	−51	0.90	....	....	.....	....	+23.0	0.4
10.000	....	....	....	....	3.5	0.40		
20.000	−37	0.60	....	....	.....	....	+17.0	0.4
25.000	....	....	− 8	0.40				
100.000	−22	0.60	....	0.35	5.0	0.60		
200.000	−12	0.50	+ 1	0.40	.....	....	+ 7.0	0.6
500.000	− 8	0.25	....	....	5.0	0.60		
700.000	....	....	+ 4	0.10				
1,000.000	....	0.30						
1,500.000	....	0.15						

the suspension. It is possible to predict from a measurement of the cataphoretic P.D. alone whether or not the suspension will remain stable. It also follows that the cataphoretic potential is the decisive one for the prevention of agglutination and, further, that this potential must be directly proportional to the rate of migration in the electric field as predicted by the Lamb-Helmholtz formula.[29]

[28] POWIS, F.: *Z. physik. Chem.*, **89** (1914–15), 191.

[29] *Cf.* LOEB: *Loc. cit.*

TABLE II.[30]—CATAPHORETIC CHARGE AND STABILITY OF SUSPENSIONS OF PARTICLES OF COLLODION

1	2 Minimum concentration required for precipitation	3 P.D. in millivolts	4 Maximal concentration at which suspension remains stable	5 P.D. in millivolts
		pH 5.8		
LiCl	M/2	(10)	M/4	17
NaCl	M/2	10	M/4	14
KCl	M/4	14	M/8	21
Na_2SO_4	M/4	13	M/8	19
$Na_4Fe(CN)_6$	M/16	13	M/32	21
$MgCl_2$	M/16	11	M/32	15
$MgSO_4$	M/16	15	M/32	19
$CaCl_2$	M/32	14	M/64	17
$LaCl_3$	M/2,048	14	M/4,096	21
		pH 11.0		
NaCl	M/2	..	M/4	18
Na_2SO_4	M/4	..	M/8	20
$Na_4Fe(CN)_6$	M/16	16	M/32	24
$CaCl_2$	M/32	15	M/64	19
		pH 3.0		
NaCl	M/2	7	M/4	14
Na_2SO_4	M/4	12	M/8	(Lost)
$CaCl_2$	M/32	16	M/64	19
$LaCl_3$	M/2,048	14	M/4,096	18
H_2SO_4	M/4	..	M/8	14

[30] LOEB, J.: *J. Gen. Physiol.*, **5** (1922–23), 123.

Precipitation by Non-electrolytes and the Mutual Precipitation of Oppositely Charged Colloids

It was noted by Linder and Picton[31] that two oppositely charged suspensions would precipitate each other if they were mixed in proper proportion. If either component were present in excess, the suspension again became stable. These observations have since been extended and confirmed for a large number of substances. In general, suspensions of the same charges do not precipitate each other. It has usually been assumed that this is also an electrical phenomenon and that agglutination occurs owing to the neutralization of the charges. As Bancroft[32]

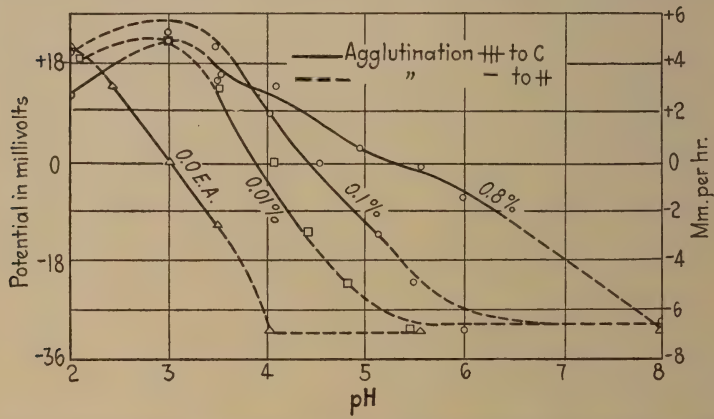

Fig. 2.—Agglutination of bacillus of rabbit septicemia by egg albumin at different pH.

has pointed out, however, the effect is not purely a neutralization one, since the relative order of flocculation of a series of positive suspensions by a series of negative suspensions is not always the same. It is evidently necessary to consider the combination as separate from the neutralization. It is possible also that the difference may be partially due to a difference in the critical potentials. Figure 2 represents the results of a series of experiments in which a suspension of bacteria was agglutinated by the addition of egg albumin. The figure shows that the agglutina-

[31] Linder, S. E. and Picton, H.: *J. Chem. Soc.*, **61, 67, 71, 87.**

[32] Bancroft, W. D.: "Applied Colloid Chemistry," New York and London, 1921, p. 226.

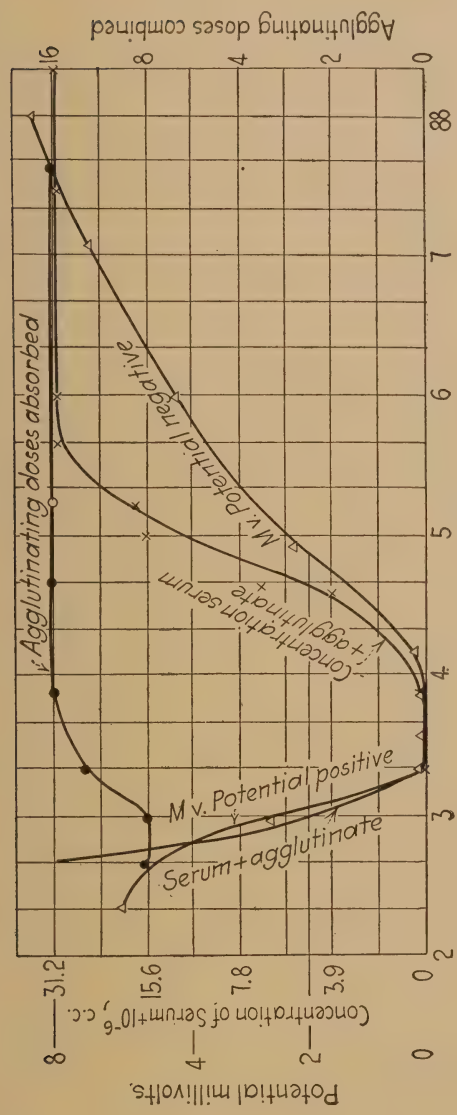

FIG. 3.—The effect of the pH on the combination of antibody and bacteria and on the potential and quantity of serum required to cause flocculation.

tion is again determined solely by the potential. It also shows that the potential of the particles is affected even where the protein has the same sign of charge as the particles, since at pH 3 the addition of the (positive) egg albumin renders the organisms still more positive. The fact that the effect of the potential is the result of the combination rather than the cause is clearly shown in Fig. 3, in which the amount of "agglutinin" combined with the bacteria at various pH is compared with the amount required to agglutinate. According to Michaelis, the antibody is positive on the acid side of pH 5.0, so that a maximum effect would be expected between this point and pH 3. This is the case with the agglutination, but no difference is noticeable in the amount of antibody combined. It will be noted that the albumin stabilizes the suspension in some pH ranges instead of agglutinating and that this effect is also due to the potential. A protective colloid and precipitating colloid can, therefore, not be separated.[33] The addition of proteins, etc., sometimes has a marked effect on the properties of a suspension by affecting the critical potential. This effect will be discussed more fully below.

As far as the writer is aware, there are no complete potential measurements in the case of the mutual precipitation of two oppositely charged suspensions, so that it cannot be determined whether or not this is also purely a question of lowering the potential below the critical value. Linder and Picton, however, showed that in the presence of an excess of one of the components the entire suspension was stable and had the charge (qualitatively) of the excess suspension, and that the flocculated suspension had a lower P.D. than either of the suspensions alone.

In the experiments discussed so far it has been possible to predict whether or not the suspension would precipitate simply by measuring the potential after the substance under investigation had been added. There are a number of cases, however, where this is not the case, and it is necessary to measure another variable. This has always been a marked property of bacterial suspensions. It was noted by Neisser and Friedemann[34] that

[33] FREUNDLICH, H. and LOENING, E.: *Fest. Kaiser Wilhelm Ges. Förderung Wiss.*, 10 jahr. Jub., 1921, 82.

[34] NEISSER, M. and FRIEDEMANN, U.: *Münch. med. Wochschr.*, 1904, No. 19.

suspensions of typhoid bacilli were not agglutinated by mono and divalent salts as were suspensions of the organism treated by immune serum. This observation was confirmed by Buxton.[35] The experiments were repeated by the writer[36] and the potential measurements were made. The results were the same as those found by Neisser and Friedemann. The experiments are shown graphically in Figs. 4 and 5. Figure 5 shows that in all cases where the potential was lowered to less than about 13 millivolts by a concentration of salt of less than 0.01 N, agglutination occurred, as would be the case with the suspensions already

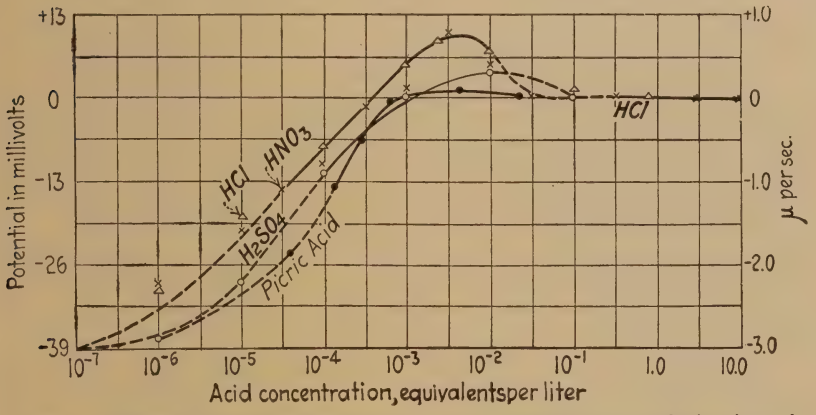

FIG. 4.—Effect of acid concentration on the potential and agglutination of suspension of *B. typhosus*.

discussed. If, however, the concentration of salt required to lower the potential to this value was 0.01 M or more, this was no longer true and no complete agglutination occurred, even though the potential was reduced to zero. It is evident that either (1) the potential measurements are wrong, or (2) some other factor has to be considered beside the potential, since with this suspension it is no longer possible to predict the flocculation from the potential alone. The fact that in the earlier experiments the potential measurements agreed so well with the flocculation results, even in high salt concentrations, renders it very improbable

[35] BUXTON, B. H.: *Z. physik. Chem.*, **57** (1907), 47.

[36] NORTHROP, J. H. and DE KRUIF, P. H.: *J. Gen. Physiol.*, **4** (1921–22), 639.

that these measurements are at fault. It may be shown directly that this is not the case by suspending the organisms in various concentrations of acid with various total salt concentrations. It is found in this experiment that the suspension at one end of the series has a low positive potential and at the other end a low negative potential. There must then be a place in between where there is no potential, even though there is a very large

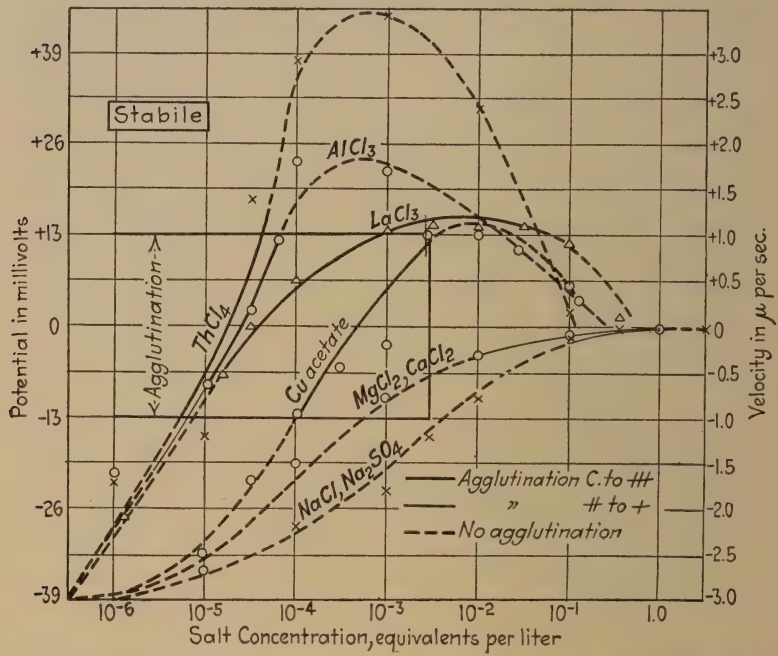

FIG. 5.—Effect of salt concentration on the potential and agglutination of suspension of *B. typhosus*.

error in the method. Nevertheless, no agglutination occurs in any tube in the presence of concentrated sodium chloride. This is shown in Fig. 6. The salt evidently acts as though it prevented the particles from sticking together, even though there is no force to hold them apart. It occurred to the writer that it might be possible to measure this sticking or cohesive force by determining the force required to separate two films of the suspension. This turned out to be the case. The measurement was made by coating two pieces of glass with a thick smear

of the suspension. The glass was then warmed slightly in order to cause the particles to adhere to it, and the two films were then allowed to rest together in the solution to be studied. The force required to tear the films apart was then determined by a torsion balance. The measurement is rough and the conditions very different from those existing in the original suspension, but nevertheless the results are surprisingly reproducible and show a very marked effect of concentrated salt solutions on this cohesive

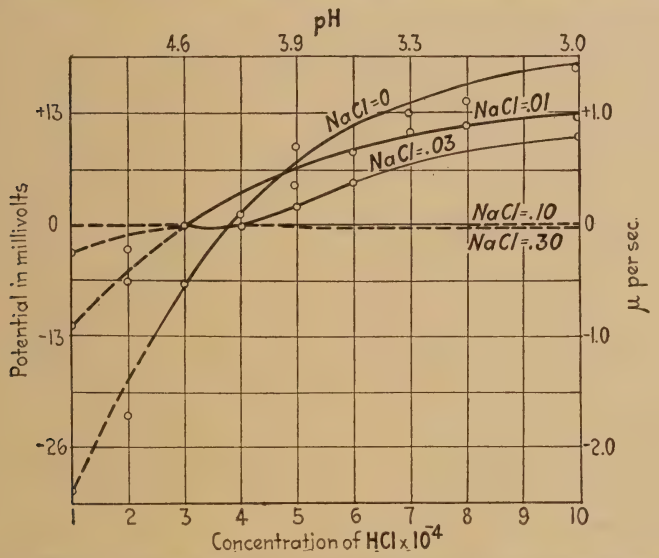

FIG. 6.—Effect of increasing NaCl concentration on the acid agglutination of *B. typhosus*.

force. Furthermore, the effect is in the range of salt concentrations where the potential measurements fail to predict the agglutination. The results of some of these experiments are shown in Fig. 7. It will be noted that the only solution which shows a second rise in this value is hydrochloric acid and this agrees with a second agglutination zone in this acid (*cf.* Fig. 5). It is evident then that so-called irregular series are not always due solely to the potential changes.[37] It may be noted that in

[37] In saturated salt solutions there is again an agglutination effect (*cf.* PORGES, O.: *Centralbl. Bact. Orig.*, **40** (1905), 133). This is probably a true solubility effect similar to that found by Loeb in the case of gelatin-coated particles to be discussed later.

the case of so-called autoagglutinable bacteria this effect of strong salt solutions does not appear. The bacteria, therefore, agglutinate in salt solutions of more than about 0.01 N without any immune serum.[38] The difference between diffuse and autoagglutinable strains of these bacteria is, therefore, the same as that between sensitized and unsensitized *B. typhosus*. The agglutinable strains and sensitized *B. typhosus* agglutinate whenever the potential is reduced below the critical value, whereas

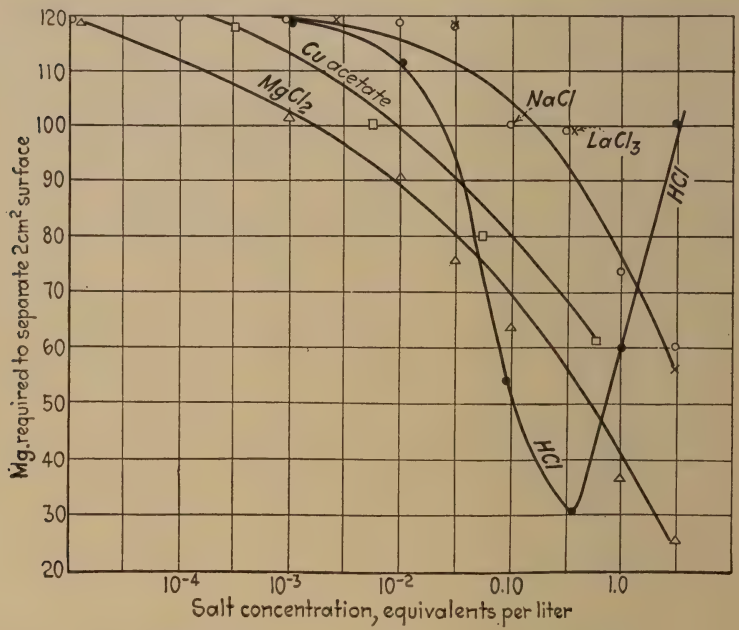

FIG. 7.—Effect of salt concentration on the "cohesive force."

in the case of the diffuse strains (or *B. typhosus* alone) the addition of concentrated salt solutions prevents agglutination by lowering the cohesive force.

It was stated above that the addition of immune serum to a suspension of bacteria caused them to act like collodion or oil particles, *i.e.*, they agglutinate whenever the P.D. is below the critical value. It might be expected, then, that the addition of serum to bacteria whose potential was already below the critical

[38] Personal communication from Dr. J. Shibley.

value would cause agglutination without any change in the potential, but an increase in the cohesive force. This is the result obtained, as is shown in Fig. 8. The figure also shows that

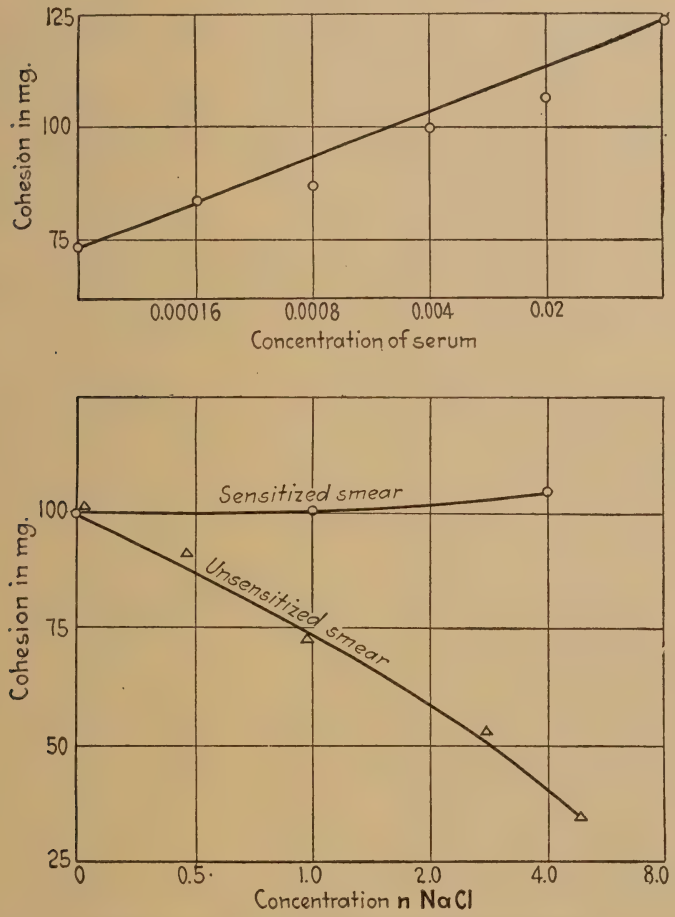

FIG. 8.—*Upper Curve.* Effect of immune serum on cohesive force in 1.0 M NaCl. *Lower Curve.* Effect of salt concentration on cohesive force of sensitized and unsensitized smears.

the cohesive force of a smear treated with immune serum is not affected by the salt concentration.

Under the ordinary conditions of bacteriological agglutination in 0.75 M salt, therefore, immune serum causes agglutination by

increasing the cohesive force between the organisms and not by affecting the potential. At the same time the antibody in the serum combines with the bacteria and probably forms a surface film. In this respect immune serum differs qualitatively from normal serum in that normal serum has no effect on the cohesive force and, hence, will not agglutinate bacteria in salt solution. It is possible, however, to arrange conditions so that agglutination is caused by a change in potential. This is the case if the suspension is near its acid agglutination point. Under these conditions both normal and immune serum will cause agglutination. It seems probable, therefore, that the reaction is due to normal serum proteins rather than to the specific antibody.

This effect of immune serum on the cohesive force has not been noted, as far as the writer is aware, in connection with any other substance. The effect of egg albumin on mastic[39] is, perhaps, similar. The reverse effect, however, is well known and is the mechanism of the protective colloid action. It was noted by Faraday that the addition of "jelly" to colloidal gold solutions prevented their precipitation by electrolytes. The action was then studied by Meyer and Lottermoser[40] who stated that "on the addition of very stable colloids, such as albumin, gelatin, agar, or gum arabic, to silver sols no precipitation is caused by electrolytes until this stable colloid is gelatinized (precipitated). The less stable silver sol is thus protected against the electrolyte by the more stable colloid. It becomes more like the latter in its behavior." Zsigmondy[41] defined the protective value of a solution as the gold number, *i.e.*, the weight in milligrams of a substance which just fails to prevent the change in color of 10 cc. of a standard gold solution on the addition of 1 cc. of 10 per cent salt. The particles in the presence of the protective colloid, therefore, act just as do the bacteria mentioned above, *i.e.*, the potential may be reduced to zero by an electrolyte and still no agglutination occurs, since there is no attractive force. If the concentration of electrolyte is still further increased until the protective colloid itself precipitates, the suspension agglutinates. This effect is

[39] Michaelis, L. and Rona, P.: *Biochem. Z.*, **2** (1906), 219.

[40] *Cf.* Taylor, W. W.: "Chemistry of Colloids," 3rd ed., New York. 1915, p. 129.

[41] Zsigmondy, R.: *Z. anal. Chem.*, **40** (1902), 697.

TABLE III.[42]—MINIMAL CONCENTRATIONS OF SALT REQUIRED TO PRECIPITATE GELATIN-COATED COLLODION PARTICLES OR GELATIN SOLUTIONS AT VARIOUS pH

pH	Salt									
	NaCl		$CaCl_2$		$LaCl_3$		Na_2SO_4		$Na_4Fe(CN)_6$	
	Particles	Solution	Particles	Solution	Particles	Solution	Particles	Solution	Particles	Solution
	M	M	M	M	M	M	M	M	M	M
3.0	2	2	>2	>2	>1	>⅞	1	½		
4.0	>2	>2	>2	>2	>1	>⅞	1	½ or above	½	7/16
4.7	>2	>2	>2	>2	>1	>⅞	1	½ or above	½	7/16
5.8	>2	>2	>2	>2	>1	>⅞	1	⅞	½	7/16
11.0	>2	>2	2	>2	...	....	1	⅞	½	7/16

[42] LOEB, J.: *J. Gen. Physiol.*, **5** (1922–23), 482, 484.

clearly shown by Loeb's experiments with collodion particles treated with gelatin (Table III). As was stated above, the precipitation of collodion particles alone is determined solely by the P.D. As Loeb pointed out, this precipitation of gelatin-coated collodion particles by high concentrations of salts is probably a phenomenon of pure solubility analogous to the salting out of proteins from solution (*cf.* below). It may be accounted for by the assumption that the salt reduces the attraction between the surface molecules of the particles and the solvent.[43]

Meyer and Lottermoser's statement that the suspension acquires the properties of the added substance has been confirmed, in general, by all subsequent investigators. There is little doubt that this is due to the formation of a surface film. It was noted by Bredig[44] that molds grow on the surface of gold particles which had been treated with gelatin. Arkwright[45] found that a suspension of *B. coli* in water containing soluble substances from *B. typhosus* was agglutinated by anti *B. typhosus* serum. This is a very sensitive test, since the action of immune serum is strictly specific. It has also been noted by a number of workers that the isoelectric point of a suspension changes to that of the added substance.[46]

It must be noted, however, as pointed out by Loeb, that the behavior of the coated particle may differ in some respects from that of the protective colloid. Collodion particles, for instance, coated with native egg albumin precipitated at the isoelectric point of egg albumin, whereas egg albumin itself does not precipitate under these conditions. Loeb suggests that the protein is denatured by the formation of the film, as has been shown to be the case at the air-liquid surface. It follows from the above mechanism of the action of protective colloids that two or three characteristics are necessary: (1) the protecting substance must

[43] LOEB, J.: *Loc. cit.*

[44] BREDIG, G.: "Anorganische Fermente," Leipzig, 1901, p. 15.

[45] ARKWRIGHT, J. A.: *J. Hygiene*, **14** (1914), 261.

[46] ARKWRIGHT, J. A.: *Loc. cit.*; COULTER, C. B.: *J. Gen. Physiol.*, **4** (1921–22), 403; LOEB, J.: *J. Gen. Physiol.*, **5** (1922–23), 109, and several earlier papers; NORTHROP, J. H. and DE KRUIF, P. H.: *J. Gen. Physiol.*, **4** (1921–22), 655.

form a surface film on the particles; (2) there must be no attractive or cohesive force between two such surface films; or (3) the resulting particle must be highly charged.

Nature of the Cohesive Force

The theory of the stability of colloidal suspensions outlined above predicts that coagulation will occur whenever the cohesive force is greater than the repulsive force. There is, in addition, very good evidence that the velocity of migration in an electric field is a measure of the repulsive force. There is every reason to believe that this rate of migration is, in turn, proportional to the potential difference between the surface of the particle and the surrounding liquid, and that the repulsive force is due to the mutual repulsion of this electric charge. The nature of the attractive force, however, is much less certain. The majority of writers on the subject state that it is a "surface tension" or "capillary" effect and Billitzer[47] assumed that the change in the potential was simply a measure of the change in the surface tension, the latter approaching a maximum as the P.D. approached a minimum. The same view is expressed by Michaelis.[48] v. Smoluchowski[49] also assumes that the attractive force is increased as the potential decreases. Freundlich[50] assumes the attractive force to be constant. If the writer's measurements of this force are significant, there is no doubt that it does not vary in any way with the potential. There is no valency effect and the effects of salt are all in concentrations so high that the potential is very low or absent. It must be noted that in Powis' experiments with oil drops there was no coalescence of the drops. There is no change in the oil-water surface, therefore, and hence it cannot be the oil-water surface tension which draws the drops together. Whatever force is active must reside in the surface film surrounding the drop, since it is these films that coalesce. There is no evidence of molecular contact of the particles.

[47] Billitzer, J.: *Z. physik. Chem.*, **51** (1905), 128.

[48] Michaelis, L.: "Die Wasserstoffionenkonzentration," 1st ed., 1914, p. 49.

[49] v. Smoluchowski, M.: *Physik. Z.*, **17** (1916), 557, 583.

[50] Freundlich, H.: *Kolloid-Z.*, **23** (1918), 163.

The Velocity of Coagulation

The changes in a coagulating suspension or sol take place relatively slowly and complete coagulation may require several hours. The change in the potential on the addition of the electrolyte, however, is almost instantaneous, at least in the suspensions of bacteria studied by the writer and also in Powis' experiments. The time element, therefore, consists in the time required for two or more particles to meet and stick together. Smoluchowski[51] has been able to derive a formula for the rate of this reaction based on the probability of collision of the particles. He assumes, as did Zsigmondy, that the particles are uncharged and that the collisions are inelastic, *i.e.*, every collision between two particles results in the formation of an aggregate of two particles. This leads to the equation

$$k = \frac{1}{t}\left(\frac{1}{\Sigma v} - \frac{1}{V_o}\right) = 4\pi D r$$

in which V_o is the number of particles present at the beginning. Σv the number present at time t, D the diffusion coefficient, and r the distance between the particles at which they are attracted. It is assumed, further, that this is not much greater than twice the radius of the particles. It may be noted that the formula is the same as that for a bimolecular reaction, with the exception that all collisions are considered as leading to combination, whereas, as is known, such an assumption will not hold with respect to chemical reactions. The theory predicts the experimental results accurately, as was found by Westgren and Reitstötter and by Kruyt and van Arkel.[52]

In the above derivation it was assumed that the particles possessed no repulsive force. This is the condition at the isoelectric point. Experimentally, however, it is known that agglutination occurs when the particles are slightly charged. Under these conditions it might be supposed that only those particles having sufficient kinetic energy would be able to approach each other within the "attraction sphere." The coagulation would be, therefore, slower but eventually would become com-

[51] v. Smoluchowski, M.: *Physik. Z.*, **17** (1916), 557, 583.

[52] Freundlich, H.: "Kapillarchemie," 2nd ed., Leipzig, 1922, p. 596.

plete, as is the case. Freundlich[53] has taken this effect into account and derived a complete formula which correctly predicts the course of the coagulation.

In certain cases—"slow coagulation"—the rate curve resembles that of an autocatalytic reaction.[54] According to v. Smoluchowski, this is a secondary phenomenon. It seems possible that this effect is due to a slow change in the potential. It was found by Powis, for instance, that there was a very rapid change in the potential immediately on the addition of the electrolyte. This was followed, however, by a second slow decrease extending over a period of days. If the potential immediately after the addition of the electrolyte were slightly above the critical value, it is readily seen that the flocculation might be caused by the second slow potential change. It is just in these cases that the peculiarity manifests itself. When the potential is reduced at once to zero, ordinary rapid coagulation occurs.

The Effect of the Nature and Valence of the Ion on the Precipitation of Suspensions

It has been noted above that precipitation of most suspensions is caused by the addition of the proper amount of electrolyte and that this effect is due to the change in either the cohesive force or the potential. The amounts of the various ions necessary to cause these effects, however, are very different. Two general statements may be made which agree fairly well with practically all experimental results: (1) The effect on the potential and stability is primarily due to the ion of the opposite charge to that of the suspension. (2) The concentration of electrolyte needed to cause precipitation decreases rapidly as the valence increases. This increase is approximately as the square of the valence—the Hardy-Schulze rule. Neither of these statements, however, is strictly true. The potential is often increased by an ion of the same charge, for instance, the addition of acid to a suspension of denatured protein which is already slightly positive, or the addition of an excess of trivalent ions. The precipitating effect, however, is due to the oppositely charged ion, as stated above.

[53] Freundlich, H.: *Kolloid-Z.*, **23** (1918), 163.
[54] Lottermoser, A.: *Kolloid-Z.*, **15** (1914), 145.

The effect is not purely a question of valence. Hydrogen and hydroxyl ions differ as a rule in their action from the other monovalent ions and behave more like the trivalent ions. The ions of the heavy metals behave differently from those of the alkalies and alkaline earths. The problem is complicated by the fact that it is difficult in many cases to vary the concentration of the ion in question without at the same time varying the hydrogen ion.

It was found by Whitney and Ober[55] that the amounts of the various ions required to cause complete precipitation of arsenic sulfide sols were chemically equivalent. This was determined by analyzing the precipitate. Equivalent amounts of the precipitating ion were bound. The same result was obtained by Duclaux.[56]

There is no simple relation, however, between the concentration of the added electrolyte and the amount combined with the particles. The results are best expressed by the exponential adsorption equation. As Freundlich has pointed out, therefore, it is not possible to determine how much electrolyte is combined with the precipitate from the total concentration of electrolyte.[57] The theory already mentioned, that the P.D. of the particles is due to a Donnan equilibrium, will account qualitatively, at least, for the experiments, in that it predicts a valency effect and a difference in the behavior of the electrolyte, depending on whether it combines with the particle or merely affects the relative concentration of ions inside and outside the particle. McTaggart's experiments with air bubbles again seem to require a separate explanation. It cannot be supposed that the air adsorbs the ion or combines with it in any way, yet the potential of these air bubbles was reversed by trivalent ions, as are most other particles. It is evident that much more quantitative work on the combination of ions with finely divided matter is necessary before any general theory can be stated.

The mechanism whereby the potential is affected by proteins, etc., is still more uncertain than in the case of electrolytes. There

[55] WHITNEY, W. R. and OBER, J. E.: *J. Am. Chem. Soc.*, **23** (1901), 842.

[56] *Cf.* TAYLOR, W. W.: "Chemistry of Colloids," 3rd ed., New York 1915, p. 109.

[57] FREUNDLICH, H.: "Kapillarchemie," 2nd ed., Leipzig, 1922, p. 581.

is every reason to believe that in this case it is a surface film formation, but whether this film is of oriented molecules, as in Langmuir's experiments,[58] or simply a concentration in the surface layer or some type of physical combination, is uncertain. It has been suggested that the combination is due to the attraction of the opposite charges, but this cannot be the decisive factor, since the addition of a positive suspension to another positive suspension can result in increasing the positive charge. It is known, on the other hand, that positive particles are retained by negative filters, whereas negative ones are allowed to pass.[59]

It may be noted, however, in cataphoresis experiments with bacteria[60] that the glass cell becomes more or less coated with bacteria which adhere firmly even in solutions in which both the glass and the bacteria are negative. It is possible that a quantitative effect could be noted if the glass and bacteria were given opposite charge, as in acid solution.

Precipitation of Native Proteins

The salting out of proteins has often been considered as analogous to the precipitation of a colloidal suspension. It has been shown by Sörensen in the case of egg albumin that this is not the case but that the phenomenon is one of ordinary solubility.[61] The same is true of the solution of casein in alkali.[62] In the precipitation of casein from solution by the addition of acid, both factors enter. The formation of insoluble isoelectric casein is regulated by the pH, as predicted by the solubility product. These particles, however, then become protected by the native protein in the solution and so do not precipitate except in a very narrow zone at the isoelectric point where the solubility of the native protein is very small.

[58] Langmuir, I.: *J. Am. Chem. Soc.*, **38** (1916), 1145.

[59] Taylor, W. W.: "Chemistry of Colloids," 3rd ed., New York, 1915, p. 59.

[60] Northrop, J. H.: *J. Gen. Physiol.*, **4** (1921–22), 633.

[61] Sörensen, S. P. L.: *Z. physiol. Chem.*, **103** (1918), 211.

[62] Cohen, E. J. and Hendry, J. L.: *J. Gen. Physiol.*, **5** (1922–23), 521.

CHAPTER IV

THE COLLOIDAL BEHAVIOR OF THE BODY FLUIDS

By

Donald D. Van Slyke

Of the substances customarily classed as "colloids," the proteins contribute the greatest part to the body material. Their part in vital processes may be no more important than that of the lipoidal colloids. The outstanding researches of Hamburger, Donnan, and Loeb have, however, given us the basis to measure and study some of the phenomena dependent on two colloidal properties possessed by many proteins, low osmotic pressure and inability to pass through membranes, and on the ability which the proteins possess, by virtue of their amino acid structure, to combine with acids and bases. The study of the behavior of body colloids other than proteins has not progressed sufficiently far to provide material for definite conclusions. For this reason we limit our discussion to the proteins, with full realization that the resulting presentation must be incomplete.

The osmotic and amphoteric properties of the proteins in water solution have been studied with a gradually increasing understanding for the past three decades. It was, however, only after Donnan's studies, of the behavior of diffusible and non-diffusible ions in solutions separated by membranes, became available that the peculiar rôle which the proteins play in controlling the distribution of other electrolytes and of water in the body could be studied in a rational manner. The application of Donnan's theory to protein solutions *in vitro* was carried out by Procter and Wilson and particularly by Loeb and his collaborators. The study has been recently extended to the animal organism by Warburg and by the writer, working with Wu and McLean. The studies thus far have been limited to the more accessible body fluids, blood and transudates. It is probable that in the

near future data will become available on the less accessible parts of the body, such as the muscles, where the work of Meyerhof indicates the buffer character of the proteins is an important factor in the cycle of muscular activity. At present, however, the discussion is practically limited, by the available material, to the blood and transudates. The following treatment of the problem is essentially that developed by Van Slyke, Wu, and McLean. We shall consider, first, the known facts concerning the relationships of electrolytes and proteins, then, their interpretation according to the physico-chemical laws of solutions, and, finally, certain deductions from the conclusions drawn.

Observed Facts Concerning the Proteins and Electrolytes of the Blood

The facts concerning the blood, which may be accepted on the basis of data already in the literature, are the following:

1. The osmotic pressure of the fluid within the cells appears to equal that of the serum outside. The disc shape of the erythrocyte indicates the absence of internal pressure. The latter would force the cell to assume a globoid shape, as it tends to do in hypotonic solutions.

2. In both cells and serum the positive charges of the alkali cations are balanced in part by negatively charged, non-diffusible protein anions, and in part by diffusible anions, of which Cl' and HCO_3' constitute the greater part.

3. All the non-protein ions normally present in amounts contributing significantly to the total osmotic pressure are monovalent. These are K^+, Na^+, Cl', and HCO_3'. Mg^{++}, Ca^{++}, SO_4'', and HPO_4'' are present in relatively such small amounts that in an approximation of conditions controlling the total osmotic pressure they may be neglected (Kramer and Tisdall, Zucker and Gutman).

4. Of the cell and serum proteins, only hemoglobin exerts a significant part of the total osmotic pressure.

That the electrolyte molecules and ions constitute nearly all of the osmotically active substances present is shown by the correspondence between the lowering of the vapor tension observed (Neuhausen) and the lowering attributable to the electrolytes

present. The chief non-electrolyte crystalloids, glucose and urea, themselves diffuse through the cell membranes and, therefore, cannot influence the water distribution. They are, furthermore, present in relatively small amounts, about 5 and 3 millimoles respectively out of a total osmolar concentration[1] of 300.

Of the proteins, it appears that hemoglobin is the only one that exerts more than 1 per cent of the total osmotic pressure in either cells or serum. Hüfner and Gansser found that electrolyte-free ox and horse hemoglobin exert the osmotic pressures calculated on the assumption that 1 molecule of oxygen combines at atmospheric pressure with 1 molecule of hemoglobin, and we have based our calculations of the osmotic effect of hemoglobin on these results. It will be seen from the tables that hemoglobin is estimated to exert about 10 per cent of the total osmolar concentration of the cells.[2]

The serum proteins, according to Starling, exert 30 to 40 mm. of pressure, or less than 1 per cent of the total (estimated at $0.300 \times \frac{311}{273} \times 22.4 \times 760 = 5{,}800$ mm.). Presumably, the cell proteins other than hemoglobin exert still less pressure, because of their small amount. It appears, therefore, that in calculating the total osmotic effects of the blood the serum proteins and the cell proteins other than hemoglobin may be neglected.

5. The cell membranes are permeable to water, carbon dioxide, to the inorganic anions, and to either H^+ or OH', or both.

In water solutions the same $[H^+]$ would result, whether the membrane is permeable to $[H^+]$, or $[OH']$, or to both. The concentration of either ion varies inversely as that of the other, according to the equation $[H^+] = \frac{K_w}{[OH']}$. Any factor which fixes

[1] We have adopted the convenient term "osmolar" concentration introduced by Warburg, to indicate the total concentration of osmotically active ions and molecules.

[2] Adair, in a personal communication, states that measurements that he has made in L. J. Henderson's laboratory indicate in dilute solutions a much higher molecular weight for hemoglobin than that found by Hüfner and Gansser, but that in concentrations approaching those in the cells other forces augment the osmotic power of the hemoglobin to about that which corresponds to Hüfner and Gansser's measurements.

$[H^+]$ therefore fixes $[OH']$, and *vice versa*, so that it is impossible, and likewise, for our present purposes, immaterial, to tell whether the membrane is permeable for $[H^+]$, $[OH']$, or both.

6. The cell membranes are impermeable to the proteins, ionized or not, and to K and Na (Gürber, Doisy and Eaton).

7. The physiological pH ranges of the cells and serum are on the alkaline side of the isoelectric points of the cell and serum proteins (Michaelis). Consequently, in the body the blood proteins combine with alkalies, but not with acids in amounts significant for the purposes of this paper.

8. The amounts of alkali bound by the cell and serum proteins increase in approximately a linear manner with increasing pH over the physiological range. The rate of change in protein-bound alkali per unit change in pH is several times as great in the cell fluid as in the serum.

9. At physiological pH ranges, reduced hemoglobin binds less alkali (0.5 to 0.7 equivalent less per molecule of hemoglobin) than does oxygenated hemoglobin.

The Solution Laws Involved in Blood Relationships

In combining the above facts to form an inclusive quantitative expression of the phenomena of electrolyte and water distribution, we have assumed for the blood the validity of the following physico-chemical laws:

1. At and near the neutral point all strong alkalies in quantitatively significant amounts are in the form of salts. At blood reaction, therefore, the total base B may be represented as BP + BA, where BP represents the alkali protein salts, in *equivalents of monovalent alkali*, and BA the salts formed by the alkali with other negative radicles, chiefly Cl' and HCO_3'.

2. The law of Donnan governing the influence of non-permeating ions on the distribution of permeating ions on the two sides of a membrane holds for the membranes of the blood cells.

3. The osmotic activity of each solute is proportional to the ratio $\frac{n}{N}$ of gram molecules of solute to gram molecules of water. The presence of the serum proteins, according to the vapor tension determinations of Neuhausen, does not affect the validity of

this ratio as the governing factor of osmotic activity, and data of Van Slyke, Wu, and McLean show that the cell proteins likewise fail to affect it. With dilute water solutions it makes relatively little difference whether the ratio $\frac{n}{H_2O}$ or $\frac{n}{\text{volume}}$ is taken as a measure or osmotic activity. In the blood cells, however, where the water constitutes only 60 to 65 per cent of the total contents, the difference is of importance.

Bjerrum (quoted by Warburg) considers the ratio $\frac{n}{N+n}$ to be a better indicator of osmotic activity in concentrated solutions than the ratio $\frac{n}{N}$. In blood, however, n is less than 0.01 as great as N, so that within the limits of experimental error it is immaterial which of these two ratios we use. Consequently, we shall employ the simpler, $\frac{n}{N}$.

For our calculations, in place of using gram molecules of water as the unit of the denominator, we have used kilos of water, in order to express the results in terms not unnecessarily removed from the familiar gram molecules per liter unit.

The relationships expressed above under (1), (2), and (3) may be expressed in certain basic equations, which, when combined, yield a practical and simple expression indicating the quantitative relationships of the factors discussed.

1. For the approximate *neutrality* of the blood reaction, $[OH']$ and $[H^+]$ being negligible compared with the other ions, we have

$$[B]_s = [BA]_s + [BP]_s \quad (1)$$

$$[B]_c = [BA]_c + [BP]_s \quad (2)$$

The brackets are used to indicate concentrations in terms of the ratio $\frac{\text{solute}}{\text{water}}$. The subscripts $_s$ and $_c$ indicate serum and cells respectively. B, BA, and BP have the significance used under (1) in the preceding discussion. (For simplicity we indicate all the alkali bound to non-diffusible acids as BP, although a small part may be bound by substances other than proteins, such as conjugated phosphates.)

2. For conformity with *Donnan's law* the *diffusible* monovalent ions have the following relationships:

$$\frac{[H^+]_s}{[H^+]_c} = \frac{[Cl']_c}{[Cl']_s} = \frac{[HCO_3']_c}{[HCO_3']_s} = \frac{[OH']_c}{[OH']_s} = \frac{[A']_c}{[A']_s} = r \qquad (3)$$

A'_c and A'_s represent the sums of all the monovalent anions. For convenience we shall use the factor r to express the ratio indicated.

$[B]_c$ and $[B]_s$ do not appear in equation (3), for they are not diffusible. If they were, in addition to the conditions defined in equations (1), (2), (3), and (4), we should be required to make our final equation conform to the condition that $\frac{[Na]_s}{[Na]_c} = \frac{[K]_s}{[K]_c} = r$, and the results would be altogether different.

3. For *osmotic equality* the ratio of osmotically active molecules and ions to water is the same in serum and cells.

$$\frac{\Sigma M_s}{H_2O_s} = \frac{\Sigma M_c}{H_2O_c} \text{ or } \Sigma[M]_s = \Sigma[M]_c \qquad (4)$$

In equation (4), M_s and M_c represent the osmotically active ions and molecules, and $\Sigma[M]_s$ and $\Sigma[M]_c$ the sums of their total concentrations, in terms of the $\frac{\text{solute}}{\text{water}}$ ratio, in serum and cells, respectively.

As alternative forms of equation (4), we may write, if we assume complete dissociation of the electrolytes:

$$[B]_s + [Cl]_s + [HCO_3]_s = [B]_c + [Cl]_c + [HCO_3]_c + [Hb]_c \qquad (5)$$

$$2[BA]_s + [BP]_s = 2[BA]_c + [BP]_c + [Hb]_c \qquad (6)$$

$$2[B]_s - [BP]_s = 2[B]_c - [BP]_c + [Hb]_c \qquad (7)$$

Equation (5) merely expresses the sum of the total ions in serum, and of ions plus hemoglobin molecules in the cells, complete dissociation being assumed, and likewise a balancing, in serum and cells, respectively, of the small amount (not over 5 per cent of the total) of osmotically active substances (PO_4'', SO_4'', etc.) not represented in the equation. Hb is expressed in units of mols of O_2 capacity.

In equation (6) the total osmolar concentration is represented as twice the molecular concentration of the salts with monovalent ions and cations (since each dissociates into two ions) plus once the concentration of base in the form of protein salt, since the

osmotic effect of BP is due to the alkali cation. In the cells we add also the osmotic effect of the hemoglobin, which is assumed to be the same regardless of the ionic charge of the hemoglobin molecules.

Equation (7) is derived from equation (6) by substituting [B] − [BP] for [BA], according to equations (1) and (2).

As stated above, equations (5), (6), and (7) are theoretically accurate if the electrolytes are completely dissociated into osmotically active ions. The observed osmotic behavior of alkali salts in general does not justify the assumption that dissociation is complete, and Neuhausen and Marshall from electrometric measurements have estimated that the sodium salts in blood serum are 83 per cent dissociated. However, if we assume, not complete dissociation, but *equal* dissociation of the salts in cells and serum, respectively, the relationships expressed in equations (5), (6), and (7) still hold, not exactly, but so nearly that the deviations may be neglected for present purposes.

The theoretical inexactness of equations (5), (6), and (7) when γ, the degree of dissociation, is less than 1, even though γ is equal on both sides of the membrane, arises as follows. When γ becomes less than 1, although [Cl], [HCO_3], and the part of [B] balanced by [Cl] and [HCO_3], are all multiplied on both sides of the equation by the same factor, $\frac{1+\gamma}{2}$, to give their osmotic activities, the part of B present as BP is multiplied by a smaller factor, γ, and the [Hb] by a larger factor, 1. The two deviating factors, γ and 1, however, are not greatly different from $\frac{1+\gamma}{2}$, which is their mean; they apply in blood to relatively small parts of the total osmotically active solutes; and they partially balance their effects, which, to judge from our experimental results, exceed but little our present limits of experimental measurement.

The basic assumptions made under (1) and (2), and expressed in equations (1), (2), and (3), stand on experimental data familiar in the literature. The assumption of equal $\frac{\text{solute}}{\text{water}}$ ratios in cells and serum, expressed under (3) in equation (4), and in equations (5), (6), and (7), is supported by the analyses of Van Slyke, Wu, and McLean (1923).

Electrolyte Distribution

Dividing equation (6) through by $2[BA]_s$ and rearranging it we obtain

$$\frac{[BA]_c}{[BA]_s} = 1 - \frac{[BP]_c + [Hb]_c - [BP]_s}{2[BA]_s} \qquad (8)$$

We may assume that, whatever the dissociations of the different salts with the monovalent anions, the salts with identical anions are dissociated to nearly the same extent in serum and cells so long as the concentrations do not differ greatly. This assumption appears justified even though the cations in the cell are nearly all K, while those in the serum are nearly all Na; for, whether conductivity or freezing point data are considered, the differences in dissociation found between potassium and sodium salts with the same anions at similar concentrations are slight. We may then write, with approximate accuracy,

$$\frac{[BA]_c}{[BA[_s} = \frac{[A']_c}{[A']_s} = r$$

From equation (3), $\frac{[A']_c}{[A']_s} = r$. From equation (1), $[BA]_s = [B]_s - [BP]_s$. Substituting, in equation (8), r for $\frac{[BA]_c}{[BA]_s}$ in the left-hand member, and $[B]_s - [BP]_s$ for $[BA]_s$ in the right-hand member, we obtain the following equation, showing *the approximate relationship between the distribution of diffusible ions and the amounts of alkali combined with the non-diffusible substances (proteins) of the cells and serum.*

$$r = \frac{[H^+]_s}{[H^+]_c} = \frac{[Cl]_c}{[Cl]_s} = \frac{[BHCO_3]_c}{[BHCO_3]_s} = 1 - \frac{[BP]_c + [Hb]_c - [BP]_s}{2([B]_s - [BP]_s)} \qquad (9)$$

We may expect the three ratios in equation (9) to vary from equality to each other, and to the r calculated from the right-hand member of the equation, in proportion as the γ, and, perhaps, secondary factors affecting osmotic activity, vary in the cells from the like factors in the serum, but we may expect these variations in the ratios not to exceed a few per cent of their values.

The experiments of Van Slyke, Wu, and McLean and of Van Slyke, Hastings, Heidelberger, and Neill with horse blood have

shown the numerical values $[BP]_c$ and $[BP]_s$ may be approximately calculated by the empirical formulas (10) and (11).

$$[BP]_s = 0.068[P]_s(pH_s - 4.80) \quad (10)$$

$$[BP]_c = 3.35[Hb]_c(pH_c - 6.74) + [O_2]_c(0.25pH_c - 1.18) \quad (11)$$

Equation (9) suffices for determining whether results obtained with a given blood agree with the quantitative requirements of the laws on which these equations are based. Because of the variation in water distribution with changing pH and oxygen content, however, the concentrations even of the non-diffusible constituents $[Hb]_c$, $[P]_s$, and $[B]_s$ are variable. Consequently, equation (9) cannot be used to predict the r curve of a given blood with varying pH. However, by combining equation (4) with (9), one is obtained in which all the values on the right side are functions of values which are constant for a given blood, *viz.*, $(B)_c$, $(B)_s$, (Hb), and $(P)_s$.

In the remainder of the chapter we shall utilize parentheses to indicate units of substance *per unit of whole blood, e.g.*, $(H_2O)_c$ = kilos of cell water per kilo of blood, $(P)_s$ = grams of serum protein per kilo of blood, and $(B)_s$ = millimols of serum base per kilo of blood, as contrasted with the bracketed $[B]_s$, which indicates the ratio $\frac{\text{serum base}}{\text{serum water}}$, or $\frac{(B)_s}{(H_2O)_s}$.

In equation (9) we substitute $\frac{(BP)_s}{(H_2O)_s}$ for $[BP]_s$, $\frac{(Hb)_c}{(H_2O)_c}$ for $[Hb]_c$, etc. We thus obtain

$$r = 1 - \frac{(H_2O)_s}{(H_2O)_c} + \frac{(BP)_c + (Hb)}{2\{(B)_s - (BP)_s\}} + \frac{(BP)_s}{2\{(B)_s - (BP)_s\}} \quad (12)$$

From equation (4) we have $\frac{(H_2O)_s}{(H_2O)_c} = \frac{\Sigma M_s}{\Sigma M_c}$. Substituting $\frac{2(B)_s - (BP)_s}{2(B)_c - (BP)_c + (Hb)_c}$ for $\frac{\Sigma M_s}{\Sigma M_c}$ (see discussion of equation (7)) we get

$$\frac{(H_2O)_s}{(H_2O)_c} = \frac{2(B)_s - (BP)_s}{2(B)_c - (BP)_c + (Hb)} \quad (13)$$

Substituting in equation (12) the value for $\frac{(H_2O)_s}{(H_2O)_c}$ from equation (13) we obtain

$$r = \frac{[H^+]_s}{[H^+]_c} = \frac{[Cl']_c}{[Cl']_s} = \frac{[HCO_3']_c}{[HCO_3']_s} = 1 - \frac{(BP)_c + (Hb)}{2(B)_c - (BP)_c + (Hb)} + \frac{(BP)_s}{2\{(B)_s - (BP)_s\}} \quad (14)$$

If the indiffusible substances, base and proteins, in the cells are assumed to maintain constant relations to each other, and the indiffusible substances within the serum are assumed to do likewise, it becomes possible to express as functions of (Hb) the other three constants, $(P)_s$, $(B)_s$, and $(B)_c$. Under these circumstances $(B)_c$ is proportional to (Hb), and the serum base and protein, $(B)_s$ and $(P)_s$, decrease by amounts proportional to (Hb). Thus, from the data in the experiments on normal horse blood by Van Slyke, Wu, and McLean, we have with a fairly close degree of constancy:

$$(B)_c = 6.0(Hb) \quad (15)$$

$$(B)_s = 148 - 8.3(Hb) \quad (16)$$

$$(P)_s = 0.072 - 0.0039(Hb) \quad (17)$$

In equations (16) and (17) the first numerical constant in each represents the average value at normal pH for serum free from cells, and when, therefore, (Hb) = 0. The second constant indicates the rates of change in $(B)_s$ and $(P)_s$, respectively, per unit of increase in hemoglobin, when the hemoglobin is measured in terms of millimols of oxygen capacity per kilo of blood.

From inspection of equation (14) it is evident that the fraction $\frac{(BP)_c + (Hb)}{2(B)_c - (BP)_c + (Hb)}$, expressing the effects of the cell factors, is at a given pH, constant for all bloods, whether of high or low hemoglobin content, as long as the ratio of base to hemoglobin in the cells remains constant, for then all the terms in both numerator and denominator vary directly as (Hb) (see equations (15) and (55)). The second fraction of equation (14), $\frac{(BP)_s}{2\{(B)_s - (BP)_s\}}$, expressing the effect of the serum factors, varies slightly, at constant pH, with the hemoglobin content of the blood.

But the variation is so small, and the total effect of this fraction on the value of r relatively so little, that the r value is, within the limits of experimental determination, independent of the hemoglobin content of the blood, even when the latter varies over such a wide range as from 3 to 12 millimolar, corresponding to from 7 to 27 cc. of oxygen capacity per 100 g. of blood.

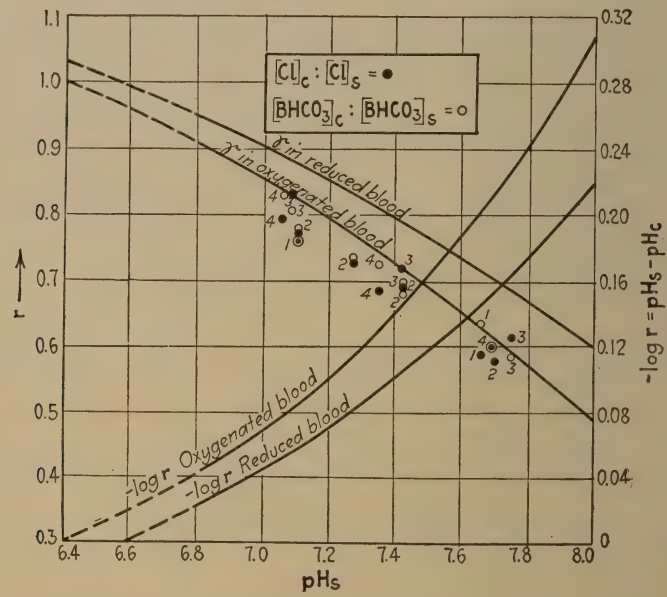

FIG. 1.—Values of $r = \frac{[H^+]_c}{[H^+]_s} = \frac{[Cl']_c}{[Cl']_s} = \frac{[HCO_3']_c}{[HCO_3']_s}$ calculated by Equation 14 for horse blood of average serum and cell composition observed in four experiments are indicated by the curves. The observed chloride and bicarbonate ratios in the experiments of Van Slyke, Wu, and McLean are indicated by the marked points.

Consequently, we may represent the average normal r, pH relationship by a single curve, which holds for bloods of varying hemoglobin content, if the other non-diffusible constituents maintain towards the hemoglobin the relationships indicated by equations (15), (16), and (17). The curves obtained by substituting in equation (14) the values of $(B)_c$ and $(B)_s$ indicated by equations (15) and (16) when (Hb) = 9, and the values of (BP)$_s$

calculated from the $(P)_s$ indicated by (17) are given in Fig. 1. Since, according to Donnan's law as expressed in equation (3), $r = \frac{[H^+]_s}{[H^+]_c}$, we may write

$$\begin{aligned} -\log r &= -\log [H^+]_s + \log [H^+]_c \\ &= pH_s - pH_c \end{aligned} \tag{18}$$

The values of $-\log r$, therefore, indicate the pH differences between the serum and cells. These values we have plotted in the curves indicated in Fig. 1.

From data of quite a different nature, obtained on whole blood, serum, and hemolyzed blood and cells, and based in part on electrometric determinations, Warburg has estimated the $pH_s - pH_c$ values in horse blood at varying pH_s. Comparison shows that our $-\log r$ curve is parallel throughout and nearly identical with the curve indicating the maximum $pH_s - pH_c$ values estimated by Warburg.[3]

Water Distribution and Cell Volume

The distribution of water between cells and serum, and the resulting volume effects, may be predicted from the pH and the degree of oxygenation of the blood if the amounts of non-diffusible substance, *viz.*, base and protein, in the cells and serum, respectively, are known, and if the law of equality of osmolar concentrations expressed in equation (4) is valid for blood.

From the general statement expressed in equation (4) we have

$$\frac{(H_2O)_s}{(H_2O)_b} = \frac{\Sigma(M)_s}{\Sigma(M)_b} = \frac{\Sigma(M)_s}{\Sigma(M)_s + \Sigma(M)_c} \tag{19}$$

$$\frac{(H_2O)_c}{(H_2O)_b} = \frac{\Sigma(M)_c}{\Sigma(M)_b} = \frac{\Sigma(M)_c}{\Sigma(M)_s + \Sigma(M)_c} \tag{20}$$

where $(H_2O)_s$, $(H_2O)_c$, and $(H_2O)_b$ represent the fractions of a kilo of water present, respectively, in the serum, cells, and whole of a kilo of blood, $\Sigma(M)_s$, $\Sigma(M)_c$, and $\Sigma(M)_b$, the total osmolar units (millimols) in the serum, cells, and whole of a kilo of blood.

[3] See Warburg, p. 230, curve I, Fig. 11.

Substituting for $\Sigma(M)_c$ and $\Sigma(M)_s$ their values as in equation (7), and replacing $(B)_c + (B)_s$ by $(B)_b$ in the resulting equations, we obtain

$$\frac{(H_2O)_s}{(H_2O)_b} = \frac{2(B)_s - (BP)_s}{2(B)_b - (BP)_s - (BP)_c + (Hb)} \tag{21}$$

$$\frac{(H_2O)_c}{(H_2O)_b} = \frac{2(B)_c - (BP)_c + (Hb)}{2(B)_b - (BP)_s - (BP)_c + (Hb)} \tag{22}$$

Multiplying equations (21) and (22) through by $(H_2O)_b$ we obtain

$$(H_2O)_s = (H_2O)_b \times \frac{2(B)_s - (BP)_s}{2(B)_b - (BP)_s - (BP)_c + (Hb)} \tag{23}$$

$$(H_2O)_c = (H_2O)_b \times \frac{2(B)_c - (BP)_c + (Hb)}{2(B)_b - (BP)_s - (BP)_c + (Hb)} \tag{24}$$

The above equations, the validity of which has been tested experimentally, enable one to predict the amounts of cell and serum water per unit weight of blood in terms which are either determinable constants $(B)_c$, $(B)_s$, and (Hb), for a given blood, or which may be calculated from such constants, *viz.*, $(P)_s$ and (Hb), and from the pH and oxygen content. The effects of pH and of oxygen saturation may be introduced as in equation (11).

Within limits, the increase of volume produced by adding a solute to a solvent approximates a linear function of the amount of solute added, and in both cells and serum nearly all the variable solute is protein. We may, therefore, with approximate accuracy write

$$\frac{V_c}{V_b} = G_b\{(H_2O)_c + m(Hb)\} \tag{25}$$

$$\frac{V_s}{V_b} = G_b\{(H_2O)_s + n(P)_s\} \tag{26}$$

where G_b is the specific gravity of the blood, with water at the same temperature as unity; m and n represent the volumes occupied in solution by a unit of cell and serum protein, respectively. When Hb and P_s are expressed in gram units, m and n both have values somewhat less than 1, since a gram of protein occupies somewhat less than 1 cc. volume. For horse blood we have found $m = 0.90$ and $n = 0.85$ when Hb and P_s are expressed

as grams of protein. When Hb is expressed in millimols of O_2 capacity, $m = 0.90 \times 0.0167 = 0.015$.

Introducing the numerical values of m and n in equations (25) and (26) we obtain

$$\frac{V_c}{V_b} = G_b\{(H_2O)_c + 0.015(Hb)\} \tag{27}$$

(Hb) being expressed in millimols of oxygen capacity per kilo of blood, and

$$\frac{V_s}{V_b} = G_b\{(H_2O)_s + 0.85(P)_s\} \tag{28}$$

$(P)_s$ being expressed as grams of serum protein per gram of blood (not, for this equation, as grams per kilo of blood).

The value of G_b and $(H_2O)_b$, constant for a given blood, may be estimated for normal horse blood as

$$G_b = 1.027 + 0.0037\ (Hb) \tag{29}$$

and

$$(H_2O)_b = 0.914 - 0.015\ (Hb) \tag{30}$$

The numerical constants in equations (29) and (30) are obtained as described in connection with equations (16) and (17), the first constant in each equation representing the G_b or (H_2O) value for normal serum, the second constant representing the change per unit increase in (Hb).

The agreement of the $(H_2O)_s$ and $(H_2O)_c$ values calculated at varying pH by equations (23) and (24) with observed values of Van Slyke, Wu, and McLean is indicated in Fig. 2.

Warburg has estimated the changes in cell volume with varying pH by measuring the oxygen capacity of the cells. The number of his determinations is sufficiently large to permit the plotting of an average curve by means of which the errors, which appear inherent in any method thus far used in estimating the small percentage changes in cell volume involved, are to a considerable extent neutralized. Warburg expresses his results in volume of cells at varying pH_s compared with the volume at pH_s 6.5. In Table I we have calculated for a blood, of the average hemoglobin content ((Hb) = 11.3 millimolar) of the bloods used by Warburg, the change in cell volume as estimated by equation (27). We have used as the unit of comparison the volume at

pH_s 6.8 instead of pH_s 6.5, for the reason that both our experimental data and Warburg's are less complete and appear less certain below pH 6.8 than above it.

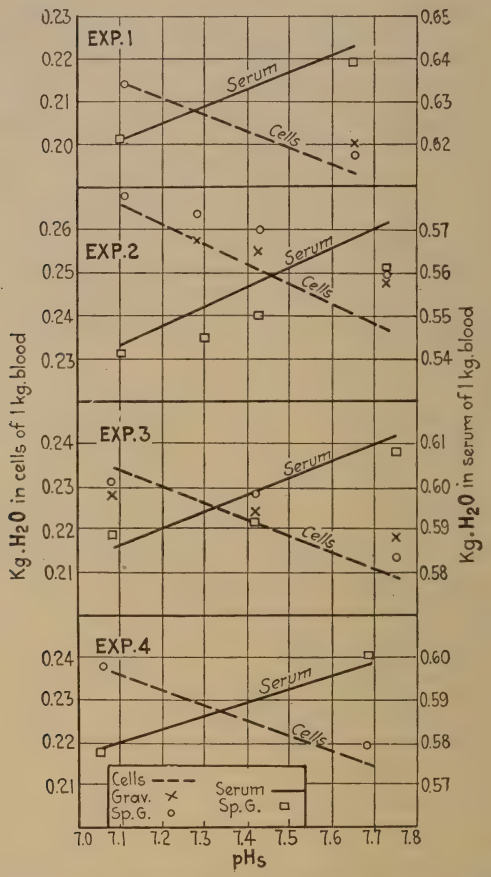

Fig. 2.—Comparison of observed and calculated water distribution. Cell and serum water contents calculated by Equations 23 and 24 are indicated by the curves. Water contents observed by the gravimetric and specific gravity methods are indicated by the marked points. (*From Van Slyke, Wu, and McLean*).

The changes observed by Warburg agree with those calculated by equation (27) within the limit of experimental error, as do the changes in Fig. 2, except in one experiment (No. 2). Warburg's observed changes tend to exceed the calculated, while those determined in our experiments tend to fall short where they

TABLE I.—CALCULATED EFFECT OF pH CHANGE ON WATER DISTRIBUTION COMPARED WITH EFFECT OBSERVED BY WARBURG

Blood constants estimated from hemoglobin content

(Hb) = 11.3 observed. $(B)_s$ = 54.2 from equation (16).
$(P)_s$ = 0.0279 from equation (17). G_b = 1.069 from equation (29).
$(B)_c$ = 67.8 from equation (15). $(H_2O)_b$ = 0.745 from equation (30).

pH_s	$-\log r$ (from Fig. 1)	pH_c	$(BP)_s$	$(BP)_c$	$\frac{V_c}{V_b}$ Calculated by equation (27)	Volume of cells in per cent of their volume at pH 6.8	
						Calculated by equation (27)	Observed by Warburg
6.8	0.04	6.76	4.2	6.5	0.640	100.0	100.0
7.0	0.07	6.93	4.6	13.4	0.631	98.6	97.4
7.2	0.10	7.10	5.0	20.4	0.621	97.0	95.2
7.4	0.14	7.26	5.3	26.9	0.611	95.5	93.7
7.6	0.18	7.42	5.7	33.4	0.602	94.0	92.2
7.8	0.22	7.58	6.1	40.0	0.591	92.3	90.5

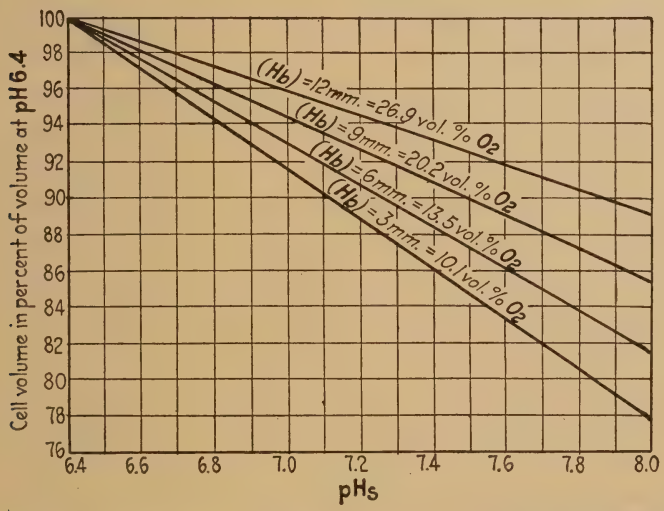

FIG. 3.—Cell volumes calculated by Equations 24 and 27 for blood of average serum and cell composition observed in experiments.

deviate from the calculated. The available data appear to agree with the predicted values as closely as may properly be expected by the limitations of present accuracy in water determinations.

In Fig. 3 the relative cell volume changes resulting from pH variations in oxygenated blood, as calculated by equation (27), are shown for bloods of varying hemoglobin content. The percentage cell volume change caused by a given pH shift is greatest when the ratio, cells: serum, is least (hemoglobin lowest), because the concentration or dilution of serum, which results from the water exchange and tends to diminish the latter, is least when the relative amount of cells is smallest.

Illustration of the Effect of CO_2 Tension Changes on the Electrolyte and Water Distribution of Oxygenated Blood

To illustrate the processes involved, we may simplify conditions by ignoring minor factors: *viz.*, the slight amounts of diffusible anions other than Cl′ and HCO_3', the osmotic and base-binding powers of the serum proteins, and the osmotic effect of the hemoglobin. We shall assume the cells to contain only base, hemoglobin, Cl, and HCO_3, and the serum to be a simple solution of bicarbonate and chloride. Equation (10) under these conditions becomes simplified to

$$r = \frac{[H^+]_s}{[H^+]_c} = \frac{[Cl']_c}{[Cl']_s} = \frac{[HCO_3']_c}{[HCO_3']_s} = 1 - \frac{[BHb]_c}{2([BCl]_s + [BHCO_3]_s)}$$

We shall assume, first, that the CO_2 tension is so low that $pH_c = 7.8$, then that it is raised so that pH falls to 6.6. According to Van Slyke, Hastings, Heidelberger, and Neill, the alkali bound by oxyhemoglobin is indicated by the equation [BHb] = 2.65 [Hb] (pH − 6.6). Assuming $[Hb]_c = 30$ millimols we, therefore, calculate at $pH_c = 7.8$ that [BHb] = 95, and at $pH_c = 6.6$ that [BHb] = 0.

In Fig. 4 we have indicated the concentrations of the positively and negatively charged ions in the cells and serum by the areas assigned to each ([Hb′] is indicated in terms of alkali equivalents bound). The concentrations of the osmotically active ions are indicated by clear areas, while that of the (relatively) osmotically inactive [Hb′] is indicated by a shaded area. For simplicity it is assumed that the ionization of each electrolyte is complete. It is also assumed that at the beginning (Fig. 4*A*) the water content of the blood is half in the cells, half in the serum.

The amounts of hemoglobin, base, chloride, and bicarbonate indicated are about those found in normal horse blood, except that the difference between $[B]_s$ and $[B]_c$ in Fig. 4*A* is somewhat exaggerated as a result of ignoring the base bound by the serum proteins and the osmotic effect of the hemoglobin.

The conditions indicated in the four diagrams of Fig. 4 are the following:

1. The conditions represented conform to the three basic laws: (*a*) in both cells and serum the positive and negative ions balance;

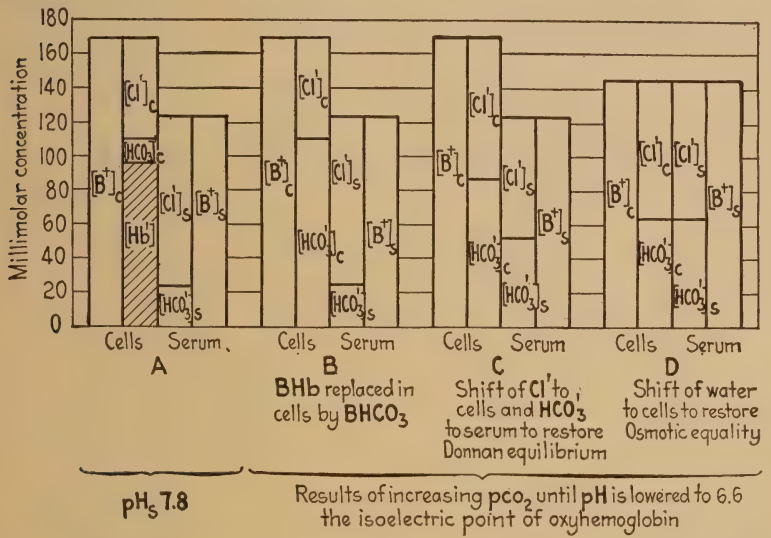

FIG. 4.—Concentrations of the positively and negatively charged ions in the cells and in the serum.

(*b*) the ratios $\frac{[Cl']_c}{[Cl']_s}$ and $\frac{[HCO_3']_c}{[HCO_3']_s}$ are equal, and conform to the simplified form of equation (10) given above; and (*c*) the osmolar concentrations obtained by adding $[B^+] + [Cl'] + [HCO_3']$ are equal in serum and cells respectively.

2. Increase of CO_2 tension has lowered the pH_c to 6.6, the isoelectric point of oxyhemoglobin. The result is that all the base formerly bound by hemoglobin as BHb has shifted to $BHCO_3$, HCO_3' replacing Hb′. In Fig. 4*B*, however, only the first of the three laws is conformed with. Positive and negative charges balance, but the greatly increased concentration of HCO_3' in the

cells obviously makes $\frac{[HCO_3]_c}{[HCO_3]_s} > \frac{[Cl]_c}{[Cl]_s}$, contrary to Donnan's law. The HCO_3' increase in the cells also causes the osmolar concentration there to exceed that in the serum. The system is not in equilibrium.

3. To restore electrolyte distribution to conformity with Donnan's law, Cl' has migrated from serum to cells, and HCO_3' in the reverse direction until again $\frac{[HCO_3]_c}{[HCO_3]_s} = \frac{[Cl]_c}{[Cl]_s}$.

4. To restore also osmotic equilibrium, water has migrated from serum to cells until the osmolar concentrations in both are

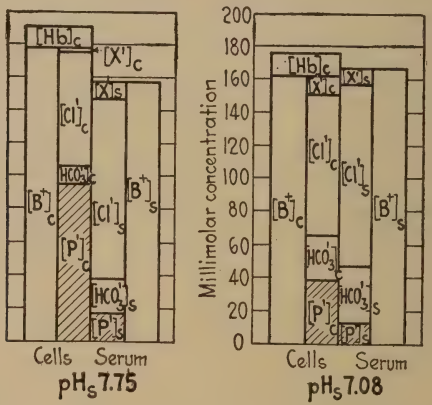

Fig. 5.—Relationships observed in defibrinated blood.

equal. Impermeability of the cell membranes to cations prevents diffusion of BCl and $BHCO_3$ from cells to serum to assist in the restoration of osmolar equality. It must all be accomplished by water transfer. The system is now in equilibrium again.

The processes represented here, for the sake of analysis, as though occurring in successive steps must in reality occur simultaneously.

The somewhat more complex changes actually occurring in blood, where the alkali-binding power of the serum proteins and the osmotic pressure of the hemoglobin enter as appreciable though minor factors, are indicated by Fig. 5, which represents data obtained from defibrinated blood. X' is used to indicate the undetermined anions.

Calculation of the Electrolyte and Water Changes in Blood During the Respiratory Cycle

We have calculated the changes that, according to our data, may be expected to accompany the CO_2 and O_2 changes of ordinary respiration.

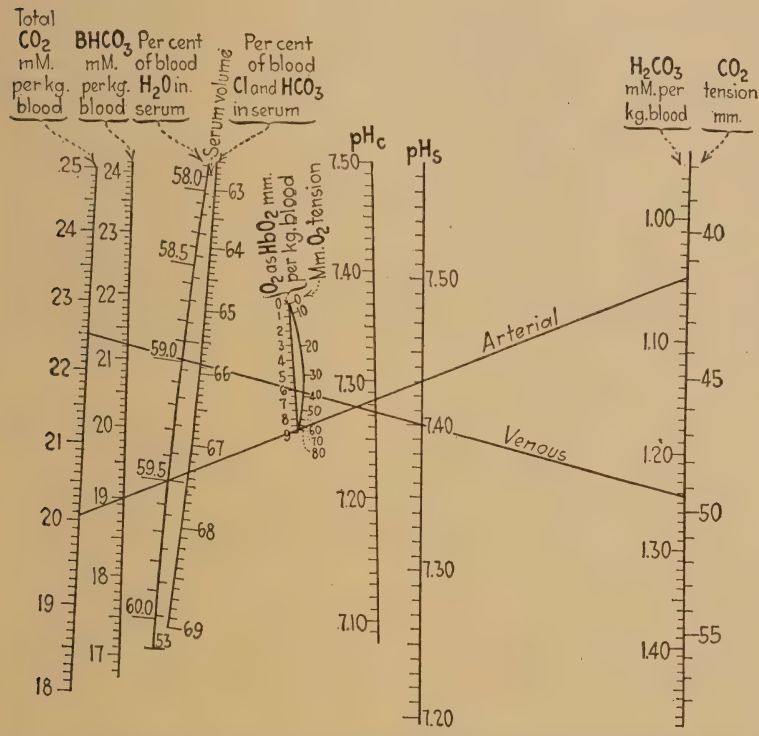

Fig. 6.—D'Ocagne-Henderson nomogram showing calculated relationships for arterial and venous blood. (*From Van Slyke, Wu, and McLean*).

In Fig. 6 we have indicated the relationships on a D'Ocagne nomogram, of a type that was devised by L. J. Henderson. A straight line, drawn across the chart, and cutting the lines representing oxygen and CO_2 tensions at any given point, cuts the lines representing $(BHCO_3)_b$, (HbO_2), pH_s, pH_c, etc., at points indicating the values these respective quantities have under the given p_{CO_2} and p_{O_2}. Such a line can be drawn because all the other variables in a given blood are dependent on these two. Over the range used, the chart is quite exact. Details of the

calculations involved in the construction of the nomogram may be obtained from the original paper of Van Slyke, Wu, and McLean. Comparison with available data, particularly of Doisy and Beckmann, for arterial and venous blood, indicates as close agreement with Fig. 4 as could be expected.

Electrolyte Distribution between Blood Serum and Transudates as a Function of the Alkali Bound by the Proteins

Loeb, Atchley and Palmer have performed experiments indicating that the membranes separating the blood serum from the fluids in the body cavities and intercellular spaces have the same permeabilities as collodion for the substances present.

Under these conditions the Donnan distribution would require expression by an equation including Na and K among the diffusible ions, instead of excluding them, as does equation (3). Expressing the distribution ratio of monovalent ions between serum and fluid as r_{sf}, the relationship would, theoretically, be

$$r_{sf} = \frac{[A']_s}{[A']_f} = \frac{[B^+]_f}{[B^+]_s} = \frac{[H^+]_f}{[H^+]_s} \tag{31}$$

when $\frac{[A']_s}{[A']_f}$ indicates the ratio of the osmotic activity of any monovalent anion, or sum of anions, in the serum to the osmotic activity of the same ion or ions in the fluid, while $\frac{]B^+]_f}{[B^+]_s}$ has a similar significance for the cations. If in place of $[B^+]_s$ and $[B^+]_f$ we substitute their values from equations (1) and (2) we obtain

$$r_{sf} = \frac{[A']_f + [BP]_f}{[A']_s + [BP]_s} \tag{32}$$

If we substitute $\frac{A_s}{r_{sf}}$ for A_f, and solve for r_{sf} we obtain

$$r_{sf} = \frac{[BP]_f + \sqrt{[BP]^2_f + 4[A]_s\,([A]_s + [BP]_s)}}{2([A]_s + [BP]_s)} \tag{33}$$

We have recalculated in Table II Loeb, Atchley, and Palmer's data, transposing the concentrations from $\frac{\text{solute}}{\text{volume}}$ to $\frac{\text{solute}}{\text{water}}$ ratios by estimating the grams of water per liter to be $990 - 0.8\ P$, where P represents grams of protein per liter. (This may be

TABLE II.—OBSERVED ELECTROLYTE DISTRIBUTION BETWEEN BLOOD SERUM AND SERUM CAVITY FLUIDS COMPARED WITH DISTRIBUTION RATIO CALCULATED FROM BASE BOUND BY PROTEINS

(Calculated from the Data of Loeb, Atchley, and Palmer)

Subject	Cl	K	Co	D	P	McA	H
Extravascular fluid	Ascitic.	Ascitic.	Ascitic.	Chest.	Ascitic.	Ascitic.	Chest.
Serum protein, gm./l.	68.000	52.000	70.000	50.000	60.000	73.000	71.000
Fluid protein, gm./l.	9.000	8.000	9.000	6.000	33.000	45.000	56.000
Estimated serum H_2O, kg./l.	0.936	0.948	0.934	0.950	0.942	0.932	0.933
Estimated fluid H_2O, kg./l.	0.982	0.984	0.983	0.985	0.964	0.954	0.945
$[P]_s$, gm./kg. H_2O	73.000	55.000	75.000	53.000	64.000	78.000	76.000
$[P]_f$, gm./kg. H_2O	9.000	8.000	9.000	6.000	34.000	47.000	59.000
$[BP]_s$, m.-Eq./kg. H_2O	12.900	9.700	13.300	9.400	11.300	13.900	13.500
$[BP]_f$, m.-Eq./kg. H_2O	1.500	1.400	1.500	1.000	6.000	9.300	10.000
$[Cl]_s$, m.-Eq./kg. H_2O	107.000	109.500	113.000	116.700	122.500	113.400	108.500
$[Cl]_f$, m.-Eq./kg. H_2O	110.200	110.800	115.700	121.500	125.600	118.000	110.500
Venous $[HCO_3]_s$, m.-Eq./kg. H_2O	29.400	25.100	28.300	28.400	17.900	30.500	32.000
Estimated arterial $[HCO_3]_s$, m.-Eq./kg. H_2O	27.400	23.100	26.300	26.400	15.900	28.500	30.000
$[HCO_3]_f$, m.-Eq./kg. H_2O	26.800	24.200	26.000	27.000	16.800	29.800	31.000
$[Na]_s$, m.-Eq./kg. H_2O	133.200	141.100	120.000	157.100	148.500	150.200	148.600
$[Na]_f$, m.-Eq./kg. H_2O	140.800	128.800	141.000	149.800	146.000	148.000	150.500
$[K]_s$, m.-Eq./kg. H_2O	4.500	5.000	2.900	3.700	5.000	5.000	4.700
$[K]_f$, m.-Eq./kg. H_2O	2.400	2.000	2.400	1.700	3.200	3.400	3.100
$[Cl]_s:[Cl]_f$, ratio	0.970	0.990	0.980	0.960	0.980	0.960	0.980
Venous $[HCO_3]_s:[HCO_3]_f$, ratio	1.100	1.040	1.080	1.050	1.070	1.020	1.030
Estimated arterial $[HCO_3]_s:[HCO_3]_f$, ratio	1.020	0.950	1.010	0.980	0.950	0.960	0.970
$[Na]_f:[Na]_s$, ratio	1.060	0.910	1.170	0.950	0.980	0.990	1.010
$[K]_f:[K]_s$, ratio	0.530	0.400	0.830	0.460	0.640	0.680	0.660
Calculated $r_{s/f}$	0.950	0.970	0.960	0.960	0.980	0.980	0.990

taken as a fairly close approximation, unless abnormal amounts of fat or other solids are present.) The $[BP]_s$ and $[BP]_f$ values are calculated on the assumption that the proteins of human serum at pH 7.4 bind the same amount of alkali per gram as the proteins of horse serum (the slight difference in pH between plasma and fluid may be neglected). At this pH the formula (equation (54)) $[BP] = 0.068\ [P]\ (pH - 4.80)$ becomes $[BP] = 0.177\ [P]$. The arterial HCO_3 values are estimated by subtracting 2 millimols per liter from the values found in the venous serum.

The estimated $[Cl]_s : [Cl]_f$ ratios found coincide with the calculated r_{sf} values nearly within the limit of experimental error. The $[HCO_3]_s : [HCO_3]_f$ ratios are all higher than the calculated r_{sf} when the venous values for $[HCO_3]_s$ are used; but the estimated arterial values for $[HCO_3]_s$ yield $[HCO_3]_s : [HCO_3]_f$ ratios which agree with the calculated r_{sf} as closely as could be expected, when the possible magnitude of the error involved in assuming a constant difference between arterial and venous CO_2 is considered.

The $[Na]_f : [Na]_s$ ratios agree, in six out of seven cases, with the calculated r_{sf} values within the rather wide limit of error assigned by the authors to the Na determination. The $[K]_f : [K]_s$ ratios are altogether lower than the calculated r_{sf}, and are very irregular. The source of the deviation and irregularity of the K ratios is at present uncertain. Considering the minute amounts of K present, it appears possible that the irrregularities may lie in the micro method used for the determination.

The irregularity of the potassium ratios, and the necessity for using estimated water and arterial HCO_3 values, make it impossible to consider the presence of a Donnan equilibrium between blood serum and edema fluid as quantitatively demonstrated with satisfactory accuracy. It appears probable nevertheless that the degree of agreement found between the calculated r_{sf} values and the ratios for Cl, HCO_3 (arterial), and Na is more than fortuitous; that it affords support for Loeb, Atchley, and Palmer's conclusion that "the relationships between serum and edema fluid result from a simple membrane equilibrium, influenced in part by the proteins present."

If the membranes separating blood serum from other extracellular fluids are permeable to all electrolytes present in amounts of quantitative importance except protein, it follows from the Donnan theory that the serum, containing more protein than the

other fluids, must, when at equilibrium with them, show a positive osmotic pressure. While the basic equations of the form of equations (1) and (2), and of equation (3) modified to include Na, hold for such a system, equation (4) and its derivatives expressing osmolar equality do not, so long as the serum volume is limited. The preponderance of the osmolar concentration even of the diffusible ions, on the side containing non-diffusing ions, when the latter are entirely on one side of the membrane and infinite volume change is excluded, has been theoretically shown by Procter and Wilson.

If the non-diffusible electrolyte (protein) also has a measurable attraction for water, the osmotic preponderance on its side of the membrane is still further increased. If serum and a transudate relatively poor in protein are separated by membranes permeable to all the non-protein ions present in quantitatively important concentrations, *viz.*, Na^+, Cl', and HCO_3', but impermeable to the protein, we may, therefore, expect the serum to exhibit a higher osmotic pressure than the edema fluid. With the osmotic pressure tending to draw water into the serum, it appears that other forces are responsible for the passage of fluid in the direction from the blood to the serous cavities and intercellular spaces.

Conclusions

Without assumption of other laws than those known to hold for physico-chemical relationships in dilute solutions, it has been possible to explain the distribution of water, chloride, and bicarbonate between the blood plasma and cells, and to predict the direction and magnitude of the shifts caused by reaction changes. The latter are completely accounted for by the changes in base bound by the proteins with changing pH. Assumptions of "hydration" or "adsorption" phenomena have not been required. There is evidence that the same laws govern the distribution of electrolytes between the blood and other body fluids, although forces other than osmosis (*e.g.*, pressure in the vascular system) play a part.

In conclusion, it is of interest to point out that, while we have information concerning the permeability of some of the body membranes to certain substances, and can thereby demonstrate

conformity of the observed diffusion phenomena with Donnan's law and the classical laws of osmosis, yet we are in entire ignorance as to the cause of some of the observed differences in permeability. We do not know why the membranes of the erythrocytes are permeable for water and anions, but not for cations.

REFERENCES

Doisy, E. A. and Eaton, E. P.: *J. Biol. Chem.*, **47** (1921), 377.

Donnan, F. G.: *Elektrochem. Z.*, **17** (1911), 572.

Gürber, A.: *Jahresb. Thierchem.*, **25** (1895), 165.

Hamburger, H. J.: *Lancet*, **2** (1921), 1039.

Hüfner, G. and Gansser, E.: *Arch. Physiol.* (1907), 209.

Kramer, B. and Tisdall, F. F.: *J. Biol. Chem.*, **53** (1922), 241.

Loeb, J.: "Proteins and the Theory of Colloidal Behavior," New York, 1922.

Loeb, R. F., Atchley, D. W. and Palmer, W. W.: *J. Gen. Physiol.*, **4** (1921–22), 591.

Michaelis, L., cited in Höber, R.: "Physikalische Chemie der Zelle und der Gewebe," Leipzig and Berlin, 1914, p. 330.

Neuhausen, B. S.: *J. Biol. Chem.*, **51** (1922), 435.

Neuhausen, B. S. and Marshall, E. K., Jr.: *J. Biol. Chem.*, **53** (1922), 365.

Procter, H. R. and Wilson, J. A.: *J. Chem. Soc.*, **109** (1916), 307.

Starling, E. H.: *J. Physiol.*, **19** (1895–96), 153.

Van Slyke, D. D., Hastings, A. B., Heidelberger, M. and Neill, J. M.: *J. Biol. Chem.*, **54** (1922), 481.

Van Slyke, D. D., Wu, H. and McLean, F. C.: *J. Biol. Chem.*, **56** (1923), 765.

Warburg, E. J.: *Biochem. J.*, **16** (1922), 153.

Zucker, T. F. and Gutman, M. B.: *Proc. Soc. Exptl. Biol. Med.*, **19** (1921–22), 169.

CHAPTER V

THE KINETICS OF DISPERSE SYSTEMS

By

E. Franklin Burton

Probably the most interesting contribution of the study of colloidal solutions to the domain of pure science has been the visual confirmation which these solutions supply to the hypotheses of the kinetic theory of matter. This latter theory, in so far as it deals with gases, has been in a fairly complete state for some time, but the difficulties inherent in the application of the kinetic theory to liquids and solids produced many doubters. In the case of the disperse systems we have, fortunately, a distribution of particles which can be rendered visible and which have supplied incontrovertible evidence of the reality of that molecular motion in liquids demanded by the kinetic theory.

From the point of view dealt with in this chapter, we shall consider the disperse systems, which are suspensions in liquid media of liquid globules or solid particles, the linear dimensions of which lie between the limits 10^{-5} and 10^{-7} cm. (or 0.1μ and $1\mu\mu$). The physical conditions which fix these two limits are: (1) for ordinary solid particles, 10^{-5} cm. is the diameter of the largest spherical particle which will remain in suspension for an unlimited time, and (2) 10^{-7} cm. is about the diameter of the smallest (supposedly spherical) particle which has been made visible by means of the most highly developed ultramicroscope. We have, then, in these systems evenly distributed clouds of small particles in a liquid atmosphere—particles small enough to be relatively comparable to molecular sizes and, consequently, small enough to partake to a noticeable extent of molecular motions.

The kinetics of these systems are important from the point of view of the following kinds of motion, which will be dealt with here: (1) the settling due to gravitation or artificially produced by centrifuging, (2) the Brownian movement—the continuous

zigzag motion of fine particles in suspension, (3) the mobility of such particles in an electrical field, due to the possession of electrical charges, and (4) a possible motion influencing their distribution, due to the mutual action of the particles.

Settling Due to Gravitation or Centrifuging

When a sphere (radius, a cm.) is moving through a liquid medium with a velocity v cm. per second, the frictional force between particle and liquid is, according to Stokes' law,[1] given by

$$F = 6\pi\eta av \text{ dynes} \qquad (1)$$

where η is the coefficient of viscosity of the liquid in the c.g.s. system. In the case of such a spherical particle falling under gravity through the liquid medium, a limiting velocity is attained when the above frictional force is just equal to the gravitational force acting on the particle, *viz.*, $\frac{4}{3}\pi a^3 (d_1 - d_2)g$, where d_1 and d_2 are the densities of the material of the particle and the medium respectively. Thus, we have, for the limiting velocity v_o, the relation

$$6\pi\eta a v_o = \frac{4}{3}\pi a^3 (d_1 - d_2)g$$

or

$$v_o = \frac{2}{9} \cdot \frac{a^2(d_1 - d_2)g}{\eta} \qquad (2)$$

The following table shows the values of v_o for various sizes of spherical silver particles, falling freely through water at ordinary room temperature, assuming the above law to hold.

Table I

Radius, centimeter	Vel. cm. per second	Time to fall 1 cm., seconds	
0.010	20.	0.0500	
0.0010	2.00	5.00	
0.00010	0.0020	500.	
0.000010	0.000020	50,000.	(½ day)
0.000001	0.0000002	5,000,000.	(58 days)

[1] *Cf.* Lamb: "Hydrodynamics," 3rd ed., 1906, pp. 551–554.

From this table it is apparent that the rate of settling for particles included within the above limits (0.1μ to 1$\mu\mu$) will be so small that it would be easily masked or neutralized by convection currents and molecular shocks. As the particles considered are taken smaller and smaller, the gravitational fall becomes less and less important in comparison with the motion caused by molecular bombardment. Measurements of such settling rates as indicated in the table may be used to determine the values of a for the particles.

By means of the centrifuge the force tending to pull the particles to the bottom of the containing vessel can be made to attain a value several times that due to gravitation. When a particle is revolving in a circle, as in the case of one of these colloidal particles in a sample which is being centrifuged, the force which must be exerted upon it in order to keep it in the same circle (say of radius r cm.) is given by

$$F_1 = m\omega^2 r$$

where ω is the angular velocity of the particle about the circle. Consequently, F_1 is a measure of the force tending to throw the particle away from the center—the so-called centrifugal force. That is, we have produced in the suspension an artificial gravitational force, tending to throw the particle to the bottom of the vessel, given by

$$F_2 = \frac{4}{3}\pi a^3(d_1 - d_2)\omega^2 r \tag{3}$$

which will produce a corresponding limiting velocity v_2 given by Stokes' law as follows:

$$v_2 = \frac{2}{9}\frac{a^2(d_1 - d_2)}{\eta}\cdot\omega^2 r \tag{4}$$

The ratio of this limiting value to that caused by gravitational settling is for the same sample:

$$\frac{v_2}{v_o} = \frac{\omega^2 r}{g} \tag{5}$$

For example, for a particle 10 cm. from the center of rotation and an r.p.m. of 1,000

$$\omega^2 r = 1.1 \times 10^5 \text{ c.g.s. units}$$

and

$$v_2 = 113 v_o.$$

From this it is apparent that the centrifuge under conditions of steady motion can be used to enhance the gravitational settling and enables one to determine the value of a from much smaller particles than in the case of gravitational settling alone.[2]

The Brownian Movement

An English botanist, Robert Brown[3] (1830), first observed that a curious zigzag motion was shown continually by small inanimate particles suspended in water. His first observations were made on pollen dust, a very fine powder which remained in suspension in water for a great length of time; similar interminable motions were afterward recognized in such suspensions as clay, powdered glass, etc. This kind of zigzag motion had been observed many years before Brown's time in suspensions of animalcules but was tacitly assumed to be a consequence of life in these small beings.

Many explanations of this motion were suggested—convection currents, external vibratory motions, light, electrical charges, surface tension, etc.—but experiment has shown that this motion is unmistakably due to resultant momentary shocks due to bombardment of the particles by the molecules of the liquid medium in the course of their ordinary thermal agitation. An application of the fundamental principles of the kinetic theory of matter enables one to calculate the displacement which a particle of given radius will undergo in any given time, in terms of the ordinary constants of the medium.

Such calculations have been carried out independently by Einstein,[4] Smoluchowski,[5] and Langevin.[6] An outline of the formula due to Einstein will be given here; the other methods have been described elsewhere. In all of these methods two fundamental assumptions are made: (1) in the motion of these particles,

[2] Svedberg: Colloid Symposium Monograph, University of Wisconsin, 1923, p. 75.

[3] Burton: "Physical Properties of Colloidal Solutions," 2nd ed., p. 51 *et seq.*

[4] Einstein: Ostwald's *Klassiker exakt. Wissen.*, **199**; *Ann. Phys.*, **4** (1905), 549; **4** (1906), 371; *Z. Elektrochem.*, **14** (1908), 235.

[5] Smoluchowski: *Bull. Intern. Acad. Sci. Cracovie*, **7** (1906), 577; *Ann. Phys.*, **4** (1906), 759.

[6] Langevin: *Compt. Rend.*, **146** (1908), 530.

the kinetic energy of the colloidal particle is equal to the mean kinetic energy of the molecules of the medium—the law of the equipartition of energy—and (2) in the resultant motion of the particles the frictional force opposing the motion is given by Stokes' law, $F = 6\pi\eta av$. The first assumption allows one to introduce the ordinary kinetic constants represented in the kinetic energy of a molecule, while the second one enables one to connect up the velocity of the particle with its radius.

Einstein's method depends upon calculating the diffusion constant D of the colloidal particles by two independent methods, and equating the two expressions. The diffusion constant is defined as follows: If we choose as the axis of x the direction of the diffusion, and if $\frac{dC}{dx}$ is the rate of change along x of C, the concentration in mols per cubic centimeter of the diffusing substance, then the quantity of dissolved substance transported per second through 1 sq. cm. perpendicular to the x axis is given by $D.\frac{dC}{dx}$ mols. That is, the coefficient D is equal to such a number of mols when the value of $\frac{dC}{dx} = 1$.

Calculation of D from Osmotic Considerations—Let a cylindrical vessel S (with axis parallel to axis of X) be divided into two parts, A and B, separated by a semi-permeable wall G (Fig.1).

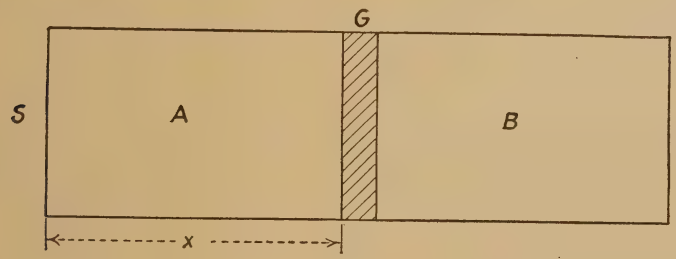

FIG. 1.

If $C_A > C_B$, force must be exerted on the wall G towards the left in order to maintain equilibrium, the size of the force per square centimeter being given by the difference between the osmotic pressures. If this force is not exerted, G will move toward the B compartment until the concentrations C_A and C_B

are equal. If the wall G is not inserted, osmotic forces will regulate the equalization of concentrations.

In Fig. 2 let the cross-section of S be 1 sq. cm. Consider the osmotic forces acting on the dissolved substance between two neighboring planes E and E' a distance dx apart. Let p and p' be the osmotic pressures at E and E' respectively. $p - p' =$ osmotic force which acts on volume $(dx \times 1)$ cc., that is, this is the force which acts on the substance dissolved in this volume. Thus $\frac{dp}{dx}$ = osmotic force on material dissolved in 1 *cc.* = say, K.

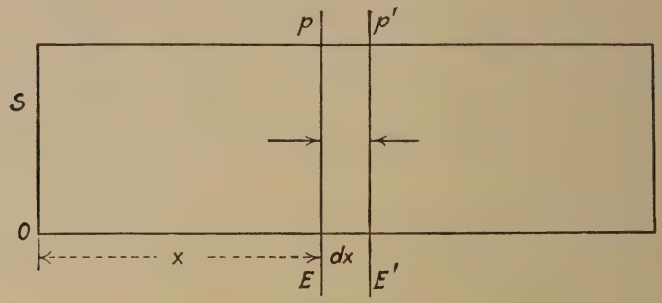

FIG. 2.

If the osmotic pressure satisfies the equation

$$p = RCT \tag{6}$$

where C = number of mols of dissolved substance per cubic centimeter of solvent, then

$$K = -\frac{dp}{dx} = -\mathrm{RT}\cdot\frac{dC}{dx} \tag{7}$$

If N = number of molecules of a substance in 1 mol, there will be NC molecules of solute per cubic centimeter of solution, and, since K is the osmotic force on all the dissolved material in 1 cc., we have the force per molecule equal to $\frac{K}{NC}$. We may treat each particle in a colloidal solution as a large molecule, and, on the kinetic view of osmotic pressure, consider the osmotic force per particle as equal on the average to the osmotic force per molecule. Therefore, $\frac{K}{NC}$ = the force due to osmosis tending to urge a given particle toward the region of increased concentration.

If the diffusing particles are spheres, large compared with molecules, we may use Stokes' expression for the frictional force, opposing the motion of such sphere, *viz.*,

$$F = 6\pi\eta a v$$

$$\text{Thus } v = \frac{F}{6\pi\eta a} = \frac{1}{6\pi\eta a} \cdot \frac{K}{NC}$$

$$= -\frac{1}{6\pi\eta a} \cdot \frac{1}{NC} \cdot \mathrm{RT} \cdot \frac{dC}{dx} \qquad (8)$$

But from the definition of the diffusion coefficient D, we have $\mathrm{D}.\frac{dC}{dx}$ = the quantity in mols of the dissolved substance which passes through a square centimeter area perpendicular to the X axis per second. This equals vC.

Therefore,

$$D \cdot \frac{dC}{dx} = C\left[\frac{1}{6\pi\eta a} \cdot \frac{1}{NC} \cdot \mathrm{RT} \cdot \frac{dC}{dx}\right]$$

and

$$D = \frac{1}{6\pi\eta a} \cdot \frac{RT}{N}. \qquad (9)$$

Calculation of D from Simple Molecular Motions.—The molecules of the medium and of the dissolved substance have a

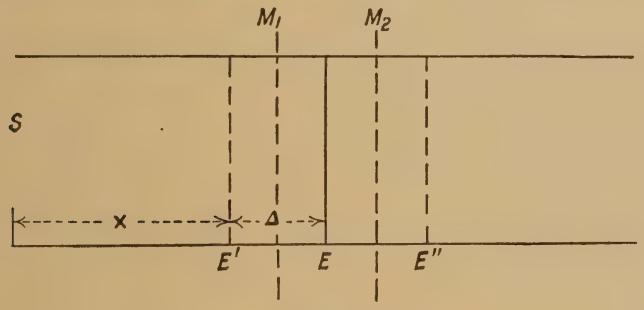

FIG. 3.

non-uniform irregular motion. Let the motion be along the axis of the same cylinder of solution, the axis of the cylinder being the axis of X (Fig. 3).

Consider particles at the plane E at time t. In a time interval, τ sec. taken so small that the distribution of concentrations does not change appreciably, these particles will have traversed distances Δ_1, Δ_2, Δ_3, etc., which are positive and negative at random.

We assume that this motion is affected by the motion of the molecules of the medium but that, on account of the dilution, there is little mutual action among the particles themselves.

The determination of the value of the diffusion coefficient D depends upon calculating how much of the material diffuses through a plane area of unit cross-section in the time τ, if the magnitude of the motion Δ parallel to the axis of the cylinder is known. Suppose the particles move an average distance Δ, one-half in a positive direction and one-half negatively. Through the plane E, there will pass only those molecules which at the beginning of the time τ are distant from E by an amount less than Δ, *i.e.*, included between the plane E' and E''.

Taking those between E and E', since one-half move to the right and one-half to the left, the number passing through E from this side will be

$$\tfrac{1}{2}C_1\Delta \tag{10}$$

where C_1 is the mean concentration in region EE', *i.e.*, the concentration at the plane M midway between E and E'.

Similarly, for the region EE'', the number passing through E in time τ will be

$$\tfrac{1}{2}\ C_2\Delta \tag{11}$$

where C_2 is the concentration along M_2.

The net diffusion through E per square centimeter in time τ is $\tfrac{1}{2}\Delta(C_1 - C_2)$ in the positive direction of X.

If the X coordinate of E is x,

$$\frac{C_2 - C_1}{\Delta} = \frac{dC}{dx}$$

Therefore,

$$C_1 - C_2 = -\Delta\frac{dC}{dx},$$

and

$$\tfrac{1}{2}\Delta(C_1 - C_2) = -\tfrac{1}{2}\Delta^2\frac{dC}{dx} \tag{12}$$

$\therefore$ The diffusion per second through unit area of E is

$$-\tfrac{1}{2}\cdot\frac{\Delta^2}{\tau}\frac{dC}{dx} = -D\frac{dC}{dx}$$

Therefore,

$$D = \tfrac{1}{2}\frac{\Delta^2}{\tau} \tag{13}$$

Combining this last equation and equation (9) we have

$$\frac{1}{6\pi\eta a} \cdot \frac{RT}{N} = \tfrac{1}{2} \frac{\Delta^2}{\tau} \tag{14}$$

which gives the general formula for the Brownian movement:

$$\Delta^2 = \frac{RT}{N} \cdot \frac{1}{3\pi\eta a} \cdot \tau \tag{15}$$

where Δ is the average distance a spherical particle of radius a will move in time τ sec. through a liquid of viscosity η.

$R = 8.31 \times 10^7$ c.g.s. units
$N = 6 \times 10^{23}$
T = absolute temperature

Space will not permit recording an account of the experimental tests of this formula carried out by various workers. The agreement between observed and calculated values is close enough to leave no doubt as to the truth of the kinetic explanation of the Brownian movement.

The Theory of Fluctuations

The kinetic explanation of the Brownian movement has received additional confirmation from the theory of fluctuations, as worked out by Smoluchowski.[7] In the ordinary treatment, when one speaks of uniformity of density and temperature in a liquid or gas, one does not consider the motion of individual molecules as being constant from molecule to molecule; one takes the average over a volume containing an immense number of molecules. Since molecular agitation intervenes in all physical phenomena, fluctuations should accompany all apparent equilibria.

Smoluchowski deduces from this theory the fluctuation in its position of a colloidal particle and obtains a formula which is in agreement with experiment.

Perrin's Distribution Law

Perrin[8] has deduced theoretically an expression for the law of distribution of colloidal particles, so as to show how the concentration of particles varies with the depth of the point below the surface. Equating the resultant osmotic effects due

[7] Smoluchowski: *Acad. des. Sc. de Cracovie*, Dec., 1907.
[8] Perrin: "Atoms" (tr. by Hammick), 2nd ed., 1923, p. 89, *et seq.*

to the particles in suspension which tend to produce uniformity of distribution to the resultant gravitational force, he obtains the formula

$$\log \frac{n}{n_o} = \frac{N}{RT} \cdot V(d - w)g(h - h_o) \qquad (16)$$

where n and n_o are number of particles per cubic centimeter at depths h and h_o below the surface, V and d are the volume and density respectively of a particle, and w is the density of liquid medium. This equation shows that the concentration of the particles of a colloidal solution should increase in an exponential fashion as a function of the depth, or, in other words, as the depth increases in arithmetical progression, the concentration of the particles should increase in geometrical progression. Perrin tested this law for depths up to 0.1 mm. and found it to hold. It is doubtful if the law holds for a much greater depth (see Burton[9] and Porter[10]).

From his measurements of values of n, h, V, and d, Perrin deduced values of N, the number of molecules in a gram molecule of a substance, which agree well with other determinations of N

Motion in an Electrical Field

If two electrodes maintained at a difference of potential are inserted in a vessel containing a colloidal solution, as a general thing the particles of the solution will move to the positive or negative pole; consequently, we say that these particles are negatively, or positively, charged. This phenomenon is not peculiar to colloidal particles in suspension, as many years ago experiments were carried out on the mobility, in an electric field, of particles of starch, platinum black, finely divided metals, graphite, quartz, etc., suspended in water and other liquids. As a result of such experiments it was found in every case when water was the suspending medium that the particles moved to the positive pole; this led to the statement that "in water all bodies appear through contact to become negatively charged, while, through rubbing against different bodies, the water becomes positively charged."

[9] Burton: *Proc. Roy. Soc* (London), **A, 100,** 705.
[10] Porter and Hedges: *Trans. Faraday Soc.*, **18** (1922), 1.

This conclusion is in keeping with the observations of the motion of water through capillary tubes or porous cups, when an electrical field is maintained through the capillary openings. In this case, the water moves toward the negative electrode, from which we conclude that the wall of the capillary becomes negatively charged while the water itself becomes positively charged, the so-called electroendosmose effect (see Perrin,[11] Elissafof,[12] Briggs-Bennett-Pierson[13]). In the case of the particles in suspension the wall moves through the liquid, while in using capillary tubes the wall is fixed while the liquid moves.

Extended work on the mobility of colloidal particles has not supported the statement quoted above; some colloidal particles move towards the positive electrode and others towards the negative electrode. Taking into consideration the recent results of many workers, we may divide colloidal solutions and suspensions into two classes, anionic and cationic, according as the particles in solution move to the anode, *i.e.*, are negatively charged, or to the cathode, *i.e.*, are positively charged.

SOLUTIONS IN WATER

Anionic	*Cationic*
1. Sulfides of arsenic, antimony, and cadmium.	1. Hydrates of iron, chromium, aluminum, copper, zirconium, cerium, and thorium.
2. Solutions of platinum, silver, gold, and mercury.	2. Bredig solutions of bismuth, lead, iron, copper.
3. Vanadium pentoxide.	3. Hoffman violet, Magdala red, methyl violet, rosaniline hydrochloride, Bismarck brown, methylene blue.
4. Stannic acid and silicic acid.	4. Albumen, hemoglobin agar.
5. Aniline blue, indigo, molybdena blue, soluble Prussian blue, eosin, fuchsin.	5. Titanic acid.
6. Iodine, sulfur, selenium, shellac, resin.	
7. Starch, mastic, caramel, lecithin, chloroform, agar-agar.	
8. Silver halides.	
9. Various oil emulsions.	

The grouping of substances in the above list suggests that in the majority of cases the so-called "charging by contact between the solid and water" is in reality intimately connected

[11] PERRIN: *J. chim. phys.*, **2** (1904), 607; **3** (1905), 50.

[12] ELISSAFOF: *Z. physik. Chem.*, **79** (1912), 385.

[13] BRIGGS, BENNETT and PIERSON: *J. Phys. Chem.*, **22** (1918), 256.

with the chemical constitution of the substances involved (see Kruyt[14]).

Various methods[15] have been used to measure experimentally the mobility of these particles in an electric field (in centimeters per second per volt per centimeter). The most satisfactory method is by means of a U-tube, such as used by Nernst, Whetham, Hardy, and others. Table II gives the values of the mobilities for various disperse systems together with calculated values of the difference of potential between the disperse phase and the medium.

It is a remarkable fact that the mobility of these colloidal particles is just about the same as that of electrolytic ions, with the exception of the fast-moving hydrogen and hydroxyl ions, although the sizes of the colloidal particles are many times the size which one usually associates with the ions. In this connection it is interesting to note that Lamb's theoretical formula for the mobility of a particle leads to the following equation:

$$V = \frac{4\pi}{K} \cdot \frac{\eta v}{X} \tag{17}$$

where

V = difference of potential between particle and liquid
K = dielectric constant of liquid
η = viscosity of liquid
X = applied electric field
v = limiting velocity of particle in the given field

From this we see that for a given V and for a given liquid medium, under constant conditions, the mobility of the particle is independent of the radius of the particle. The above formula is deduced by equating the electrical force acting on the particle to the fractional resistance as given by Stokes' law, and, consequently, will be true only for particles for which Stokes' law is applicable, *i.e.*, for particles the diameters of which are large compared to the mean free path of the liquid molecule. This suggests that the ordinary electrolytic ion is an entity to which Stokes' law may be applied.

[14] KRUYT: *Nature*, June 16 (1923), 827.

[15] BURTON: "Physical Properties of Colloidal Solutions," 2nd ed., p. 132, *et seq.*

TABLE II.—MOBILITIES OF THE DISPERSE PHASE IN VARIOUS AQUEOUS SOLUTIONS

Disperse phase	Mobility in centimeter per second per volt per centimeter $\times 10^{-5}$	P.D. in volts between the disperse phase and medium	Authority
Suspensions:			
Lycopodium	−25.0	−0.035	Quincke
Quartz	−30.0	−0.042	Whitney and Blake
Air bubbles	−40.0	−0.056	McTaggart
Suspensoids:			
Arsenious sulfide	−22.0	−0.031	Linder and Picton
Prussian blue	−40.0	−0.056	Whitney and Blake
Prussian blue	−41.5	−0.058	Burton
Gold (chem. prep.)	−40.0	−0.056	Whitney and Blake
Gold (chem. prep.)	−7.1 to −57.4	.....	Galecki
Gold (chem. prep. and Bredig)	−26.0	−0.036	Rolla
Gold (Bredig)	−21.6	−0.030	Burton
Platinum	−30.0	−0.042	Whitney and Blake
Platinum (Bredig)	−24.0	−0.034	Rolla
Platinum (Bredig)	−20.3	−0.028	Burton
Platinum (Bredig)	−20.0 to −40.0	.....	Svedberg
Silver (Bredig)	−32.0 to −38.0	.....	Cotton and Mouton
Silver (Bredig)	−20.0	−0.028	Svedberg
Mercury (Bredig)	−25.0	−0.035	Burton
Silver (Bredig)	−23.6	−0.033	Burton
Bismuth (Bredig)	11.0	0.015	Burton
Lead (Bredig)	12.0	0.017	Burton
Iron (Bredig)	19.0	0.027	Burton
Ferric hydroxide	30.0	0.042	Whitney and Blake
Ferric hydroxide	52.5	0.073	Burton
HA Globulin	−19.8 to −22.9	−0.031	Hardy
HCl Globulin	− 9.0 to −11.5	−0.015	Hardy
NaOH Globulin	7.7	0.100	Hardy
H_2SO_4 Globulin	−18.5	−0.026	Hardy
H_3PO_4 Globulin	−23.0	−0.032	Hardy
Emulsions:			
Hydrocarbon oil	−43.0	−0.060	Lewis
Spec. acid-free oil	−37.2	−0.052	Ellis
Acid-free oil	−32.4	−0.045	Ellis
Liquid paraffin	−29.3	−0.041	Ellis
Cylinder oil	−27.0	−0.038	Ellis
Water-soluble oil	−48.0	−0.067	Ellis
Aniline, fresh distilled	−31.1	−0.043	Ellis
Chloroform	−10.0	−0.014	Ellis
Gummigutt	−18.1	−0.025	Ellis
Mastixharz	−17.7	−0.024	Ellis
Electrolytic ions:			
Organic compounds (high molecular weight)	20.0		
Hydrogen (+)	329.0		
Hydroxide (−)	180.0		
Chlorine (−)	68.0		

Experiments carried out by Currie[16] to test the influence of the viscosity of the medium on the mobility of electrolytic ions and colloidal particles show that the value of v is always such that ηv is constant for given solutions with fixed value of X.

The existence of this mobility of particles in an electric field raises in our minds the question of the mechanism by which these particles become charged. On the one hand, we have the purely mechanical suggestion of "charging by contact"—words used as a cloak for ignorance. At the other extreme we have Loeb[17] maintaining that the whole action is explicable as a purely classical chemical reaction. Whatever the language used, we must recognize that the possession of a negative charge by a surface of a wall (or of a particle) means the existence of a supernormal collection of electrons on that surface, while the possession of a positive charge means a corresponding deficiency in electrons. This derangement of the normal distribution of electrons may, in the case of contact of two solids, *e.g.*, fur and ebonite, be due to the direct transfer of electrons from one body to the other; however, in the case of contact between solid and liquid, since the transfer of charges takes place by means of the motion of ions, the most rational explanation seems to be that the solid surface becomes charged by means of an absorption of ions of one sign—a result which may be brought about by the interposition of a chemical reaction at the surface or by a mere selective adsorption of one kind of ion by the solid surface. Loeb seems to push his results too far when he denies the existence of surface adsorption in solid colloidal particles merely because the water-permeable protein particles with which he experiments indicate quite conclusively the existence in them of a reaction throughout their whole volume (see McBain[18] on soaps).

Coagulation of Sols by Electrolytes[19]

The separation of colloidal solutions into suspensoids and emulsoids is markedly justified by wide differences in sensitiveness to added electrolytes. As a general rule, suspensoids are

[16] To be published.

[17] Loeb: "Proteins and the Theory of Colloidal Behavior," 1922.

[18] McBain: Third Coll. Chem. Report Brit. Assoc., 1920, p. 2.

[19] Burton: "Physical Properties of Colloidal Solutions," 2nd ed., p. 155, *et seq.*

precipitated by extremely small additions of electrolytes, while the emulsoids are affected by comparatively strong solutions only.

Coagulative Powers of Electrolytes.—To a given volume of colloidal solution is added a quantity of electrolyte sufficient to produce coagulation (precipitation) of the disperse phase; if the molecular concentration of the electrolyte in the mixture be c, then $\frac{1}{c}$ is called the coagulating power of the given electrolyte on the given sample of the colloid. Among several samples of the same colloid one should express the coagulating powers of different electrolytes in terms of the necessary concentration per gram of the disperse phase per cubic centimeter of sol.

Two remarkable results are evident on comparing the coagulative powers of various electrolytes on colloids of different kinds; first, the coagulation depends almost entirely on the ion bearing a charge of sign opposite to that of the colloidal particle, and second, with solutions of salts trivalent ions have, in general, immensely greater coagulative power than divalent ions, and the latter, in turn, much greater than univalent. Acids and alkalies in particular cases act more strongly than the corresponding salts.

Systematic work on this phenomenon was first undertaken by Schulze, and Linder and Picton, from a chemical point of view. The coagulative powers of different salt solutions were determined by the former for arsenious sulfide and antimony sulfide, and by Linder and Picton for arsenious sulfide; their conclusion was that this coagulative power depended solely on the valency of the metal ion, *i.e.*, the ion bearing a charge opposite to that on the sulfide particle.

On examination of the results of experiments of coagulative powers, one is struck by the remarkable differences which, as a general rule, are apparent in the coagulating powers of univalent, divalent, and trivalent ions. The earlier workers apparently looked upon the differences existing between two different ions of the same valency as experimental errors and were led to suggest the two laws indicated above: (1) that the coagulating power of an electrolyte depended only on the ion bearing a charge opposite in sign to that on the colloidal particle, and (2) that the powers of univalent, divalent, and trivalent ions were in the ratios which may be expressed, as suggested by Whetham, by the ratios

$1 : x : x^2$, where x is a constant. As much of the early work on coagulation seems to support this result, it has come to be called the Schulze-Linder-Picton law of coagulation. Taking the averages of recorded results, we have the following numbers for the ratios:

Linder and Picton	1: 63:863
Freundlich	1:104:810
Schulze	1: 49:810

which only approximate to the Whetham suggestion of $1 : x : x^2$.

Electrokinetic Effects of Added Electrolytes.[20]—Jevons first suggested that the coagulating action of electrolytes was due to the neutralization of a charge possessed by the particles. Hardy found that globulin solutions were most easily coagulated at the point where their charge was zero, *i.e.*, at the time when they showed no motion in an electric field (the isoelectric point). Following Hardy's suggestion, experiments were carried out by the writer to determine the influence of added electrolytes on the mobilities of the particles of gold, silver, and copper Bredig solutions.

Billiter, in making similar experiments on colloidal solutions of platinum, mercury, silver, gold, and palladium, to which he added gradually increasing amounts of various electrolytes, found that the mobility of the particle gradually decreased and eventually changed in direction, showing that even the sign of the charge was changed by the addition of the electrolyte. He added gelatin and urea to his solutions in order to prevent coagulation. Whitney and Blake disagreed *in toto* with the conclusions of Billiter, and failed to reproduce his results with colloidal solutions of gold and platinum, free from gelatin. They assigned Billiter's change in the direction of migration to the dissolved gelatin.

Exhaustive experiments carried out by the writer on solutions of gold, silver, and copper showed conclusively that the addition of electrolytes caused a reduction of the mobility of the particles; as the mobility approached zero, the coagulation by the electrolyte became more rapid. The amount of reduction in the mobility ran directly parallel with the coagulative power of the

[20] BURTON: "Physical Properties of Colloidal Solutions," 2nd ed., p. 163, *et seq.*

electrolyte, which showed that the coagulation was primarily due to the discharge of the particles, particularly with divalent and trivalent ions as the active coagulants.

The relation of electrolytes to the mobility of particles is exactly the same as the action of the same electrolytes in reducing the electroendosmose effects in capillary tubes (see Perrin, Elissafof, and Briggs[21]).

Mutual Action of Colloidal Particles

In spite of the opposition expressed by some authors, in the opinion of the writer there does exist a mutual action of colloidal particles, in a given solution, due to the charge possessed by the particles. The fact that a solution containing particles charged with one sign, say positive, when added to a solution of particles charged with the opposite sign (−), invariably produces mutual coagulation shows that the individual particles can come within a region of mutual action. We cannot look upon the Helmholtz double layer as anything more than a state of affairs brought about by the charged particle, whereby we have near the particle a slightly increased concentration of ions bearing a charge opposite to that on the particle. This ionic atmosphere will be graded off to the general concentration in the bulk of the medium. The linear extent of this graded ionic atmosphere may be easily of the same order as the distance between the particles—a condition which would induce a mutual repulsion of the particles. The simplest explanation of the uniform distribution of colloidal particles in a given sample is the mutual repulsion due to the electric charges.

There are two very definite proofs that there is a mutual action of the particles of a given colloidal solution. In the first place, observation with the ultramicroscope will force one to the conclusion that the particles do not come into collision with one another; two neighboring particles may approach and rotate about a common center for a short time, but they will always separate before a collision takes place.

In the second place, the experimental evidence that the particles in a given solution are uniformly distributed throughout the solution seems quite conclusive (Burton,[22] Burton and

[21] *Loc. cit.*, nos. 11, 12, 13.

[22] Burton and Bishop: *J. Phys. Chem.* (1921).

Currie[23]). Not only so, but for any given material in the particles, with given conditions of electrolytic content in the medium and given conditions as to gravitational force (including that induced by centrifuging), there seems to be a limiting concentration of the disperse phase. In the case of silver sol, the writer found that the limiting concentration was such that the nearest distance of approach of two silver particles was of the order of 50 times the diameter of the particle. On attempting to concentrate the sol further, some of the disperse phase was forced out of the solution; the amount of electrolyte present in the sample was so small that its concentration during the process could not account for the change in disperse phase kept in suspension.

The establishing of the existence of this mutual action leads to several important inferences. It endows the particle with an effective charge capable of reacting with a like charge on neighboring particles and also capable of inducing motion in an electric field, thus offering an explanation of cataphoresis much more satisfactory than that given by Helmholtz.[24]

More important still is the bearing of this mutual action on the application of the osmotic pressure formula, $Pv = \mathrm{RT}$, to these solutions. This formula is taken over from the kinetic theory of gases and, consequently, this mutual action can be introduced in the same manner as one would introduce a correction for a mutual action of the molecules in a gas. This mutual action can be taken account of by adding to the equation expressing the energy of the particles the virial of the mutual forces.[25] We have

$$\tfrac{1}{2}\Sigma m V^2 = \tfrac{3}{2}Pv + \tfrac{1}{2}\Sigma r F(r) \qquad (18)$$

where

m = mass of molecule
V = velocity of molecule
P = pressure of gas
v = volume of gas
r = distance between two molecules
$F(r)$ = law of force between two molecules

[23] Burton and Currie: To be published later.

[24] Helmholtz: *Ann. Phys.*, **7** (1879), 337; *Memoirs Lon. Phys. Soc.* (1888).

[25] Rayleigh: Sci. Papers, **5**, no. 304, p. 238.

Putting $\frac{1}{2}\Sigma mV^2 = \mathrm{RT}$ for one molecular weight, we have for P:

$$P = \tfrac{2}{3}\mathrm{RT}.\frac{1}{v} - \tfrac{1}{2}\frac{1}{v}\Sigma rF(r) \qquad (19)$$

Whenever the osmotic pressure is treated as a gas pressure, as, for example, in deducing the formula for the Brownian movement or in Perrin's distribution law, the value of P will involve not only RT as usually used, but also the virial term.

In the case of the Brownian movement this connection indicates that the intensity of the movement depends, to a certain extent, on the charge possessed by the particle. A particle which is charged and in an atmosphere of similarly charged particles will have a greater Brownian movement velocity than if the particles were uncharged. It is on record that when electrolytes are added to a sample of colloidal solution under the ultramicroscope the Brownian movement is reduced even before coagulation sets in.[26,27]

Summary

Summarizing the foregoing, we may draw attention to the following important kinetic relation of these disperse systems:

1. The particles are of such a size as to possess a very small limiting velocity under gravitation and have supplied most interesting examples of the application of Stokes' law.

2. The Brownian movement affords the best direct optical evidence we have of the existence of molecular motions in liquids and gases.

3. The possession of an electric charge by the particles offers exceptional opportunity for studying the actions of electrolytic ions, both from the point of view of the mobility of the particles in an electric field and from the phenomena of coagulation.

4. The mutual action of the particles, whether from their relation to surface tension or electrical repulsion, opens up a very promising field of study.

[26] Maltézos: *Ann. chim. Phys.*, **7** (1894), 559; *Compt. Rend.*, **121** (1895), 303.

[27] Henri: *Bull. Soc. Fr. Phys.*, **4** (1908), 45.

CHAPTER VI

SURFACE ENERGY IN COLLOID SYSTEMS

By

William D. Harkins

That heat is taken up by a liquid when it is vaporized at a constant temperature is recognized as an every-day phenomenon. The heat added is, in general, much greater than that which is equivalent to the work done by the vapor in pushing away the atmosphere. The vaporization of water into a vacuum at 10°C. requires the addition of 10,000 cal. of heat per gram molecule of water, or 4.18×10^{11} ergs. Thus, the average energy utilized in separating one molecule from the neighboring molecules which surround it, when it is inside the liquid phase, amounts to the number of ergs per gram molecule, as given above, divided by the number of molecules in a gram molecule (6.06×10^{23}), or 69.6×10^{-14} ergs.

Since energy is thus absorbed in separating a molecule completely, as in vaporization, it is natural to conclude that energy must be added to a system if some of its molecules are to be partly separated from those surrounding them, as when a new surface area is formed. That at least a part of this energy may be added in the form of work is indicated by an arrangement suggested by Maxwell (Fig. 1).

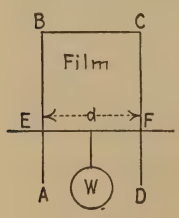

Fig. 1.

A soap film is stretched between the upper part of a wire frame *ABCD* and a movable cross wire *EF*. If the wire *EF* is very light, the film will contract to a very small area, but it is found that, if weighted to a definite weight *W*, the wire will keep the film extended to its initial area. In this case, the tension of the two sides of the film along *EF* is equal to the pull of the weight

W. The surface tension (γ) of the liquid is the pull exerted by one side of the film along a unit length, or

$$\gamma \cdot 2d = mg \qquad \text{so} \qquad \gamma = \frac{mg}{2d} \tag{1}$$

If the magnitude of the weight necessary to keep the film extended is independent of its area, the surface is considered as *saturated;* that is, a saturated film is one whose surface tension is independent of its extension. The surface of any pure liquid is saturated if the surface itself is pure. Certain solutions also have saturated surfaces, as is practically the case for aqueous solutions of sodium oleate at concentrations between 0.01 and 0.1 M. The interface between benzol and an aqueous solution of this salt is saturated between 0.015 and 0.1 M.

Though the distinction between saturated and non-saturated surfaces is an important one, it is customary to restrict the treatment of surface energy relations almost entirely to saturated surfaces. Unsaturated surfaces are frequently found on solutions, and they may occur with a pure liquid if it is spread into a sufficiently thin sheet. Recent theory indicates, however, that such a sheet must be exceedingly thin—so thin that such films are seldom formed. In the treatment which follows, all films will be considered as saturated unless otherwise specified.

For such surfaces, the work of extension is equal to the force which produces the extension, multiplied by the distance through which the force acts, so the work in ergs necessary to produce a unit area of surface is numerically equal to the number of dynes which expresses the surface tension. Since this work may be entirely given back in the contraction of the surface, this amount of energy is said to be present in the surface as *free energy*. If γ is the numerical value of the surface tension, then the surface tension of the liquid is γ dynes per centimeter, and its free surface energy is γ ergs per centimeter.

Table I gives the surface tension and the free surface energy of a number of liquids at 20°C.

One of the most important characteristics of surfaces is that the surface tension, or the free surface energy, decreases rapidly as the temperature increases, and becomes equal to zero at the critical temperature. This decrease is often linear, as illustrated

in curve 2 (Fig. 2), although curves of the forms designated as 1 and 3 often occur.

TABLE I.—SURFACE TENSION AND THE FREE SURFACE ENERGY OF A FEW TYPICAL LIQUIDS

	γ_o	$l = 273\frac{d\gamma}{dt}$	E_s	$S = \frac{d\gamma}{dt}$	$\frac{\frac{d\gamma}{dt}}{\gamma_o}$
Water	75.87	42.25	118.10	0.1511	0.00199
Bromine	51.00	144.50	195.50	0.5300	0.01040
Sulfur	60.27	3.82	64.09	0.0140	0.00023
Carbon disulfide	37.71	43.91	81.60	0.1607	0.00426
Mercury	480.30	60.10	540.40	.....	0.00046
Hexane	21.31	28.15	49.50	0.1032	0.00484
Octane	23.36	25.04	48.40	0.0920	0.00394
Chloroform	28.77	30.94	59.70	0.1134	0.00394
Ethyl iodide	33.53	37.51	71.00	0.1370	0.00409
Methyl alcohol	23.50	19.40	42.90	0.0710	0.00306
Ethyl alcohol	23.30	21.70	45.00	0.0800	0.00343
Glycol	49.34	24.52	73.90	0.0935	0.00189
Glycerin	65.28	16.35	81.60	0.0598	0.00096
Benzol	31.55	35.64	67.20	0.1300	0.00413
Toluene	30.76	31.32	62.10	0.1150	0.00373
Cymene	30.18	26.57	56.70	0.0980	0.00323
Diphenyl	40.41	24.88	65.30	0.0911	0.00225
Phenol	42.27	28.62	70.90	0.1050	0.00248

The principle of Le Chatelier indicates that when the state of a system in equilibrium is varied, the system changes in such a way as to oppose a greater resistance to the change. Thus, if the surface is expanded, an increased resistance to further expansion would be introduced, provided the surface should become cooler, since this would raise the surface tension. From this, it may be deduced that a surface cools if it is extended, or in such a case the initial temperature may be restored if heat is added. The amount of heat required per unit area of extension of the surface is called the latent heat[1] of the surface.

According to the equation of Clapeyron, first applied to surfaces by Lord Kelvin, the latent heat of the surface is given by the equation

$$l = -T\frac{\partial\gamma}{\partial T} = -\frac{\partial\gamma}{\partial lnT} \qquad (2)$$

Thus, the latent heat of the surface is equal to the absolute temperature multiplied by the negative of the rate of change of the surface tension with the temperature.

The total energy (u) of the surface is, therefore,

$$u = \gamma + l \qquad \text{or} \qquad u = \gamma - T\frac{\partial \gamma}{\partial T} \tag{3}$$

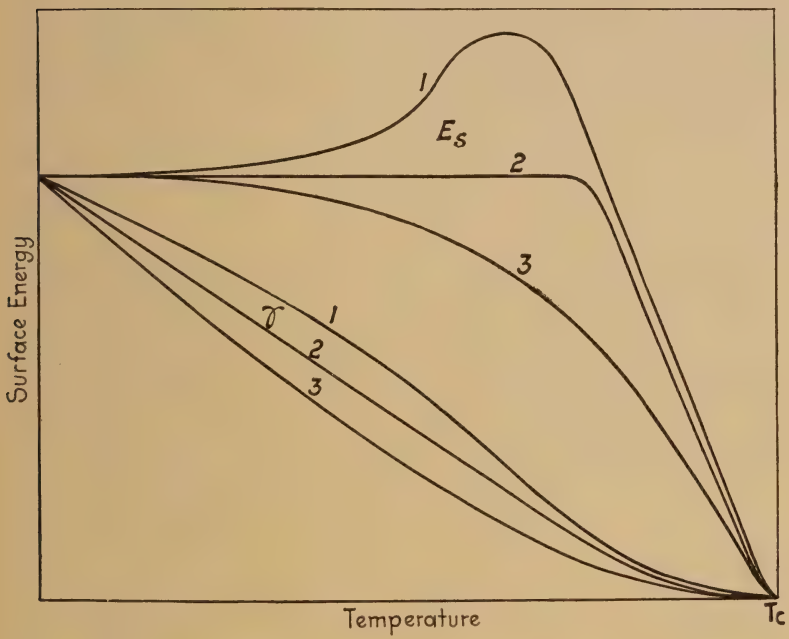

FIG. 2.—The free energy (γ) and the total energy (E_s) or (μ) of liquids.

Now, if γ is a linear function of the temperature, as it often is, $\frac{\partial \gamma}{\partial T}$ is constant, or the latent heat of the surface is proportional to the absolute temperature. In this case, l increases at the same rate at which γ decreases, or

$$u = l + \gamma = \text{constant} \tag{3}$$

when γ is a linear function of T.

The entropy of the surface S is equal to the latent heat of the surface divided by the temperature, or

$$S = \frac{l}{T} = -\frac{T}{T}\frac{\partial \gamma}{\partial T} = -\frac{\partial \gamma}{\partial T} \tag{4}$$

so

$$S = \text{constant}$$

when γ is a linear function of T. (4′)

At low temperatures, the latent heat of the surface is small, and the surface energy consists largely of the free surface energy. At temperatures nearly as high as the critical temperature, the free surface energy becomes very small and the latent heat relatively large, so in this region the surface energy is largely contributed by the heat motion of the molecules. At the critical temperature the surface energy becomes equal to zero, or

$$\begin{aligned} V &= 0 \quad \text{at} \quad T = T_c \\ l &= 0 \\ u &= \gamma + l = 0 \end{aligned} \tag{3″}$$

This indicates that the surface tension (γ) curve becomes tangent to the temperature axis at the critical temperature.

Figure 3 illustrates a molecule A which is in the surface of a liquid. This is attracted in all directions except upward, so the only entirely unbalanced attraction is that which is downward. A molecule which rises into the surface against this attraction increases its potential energy. At least, the greater part, and presumably nearly all, of the surface energy is present in this potential form. A molecule may rise into such a position against this attraction by a utilization of a part of its own kinetic energy, but in order that the surface area shall be increased by this process, the surface must at the same time be expanded by a force which contributes free energy. According to this point of view, while the energy of the surface is largely potential, it may be contributed to the surface by (1) the heat motion of the molecules, or (2) work done by forces from the exterior. It is of interest to note that, in order that a molecule may get into the surface, the average energy contributed from the heat motion of the molecules is 144 per cent of the mean energy of translation of a gas molecule at that temperature. That is, in general, only those molecules, the kinetic energy of which is greater than the mean, possess enough energy of translation to rise into the surface.

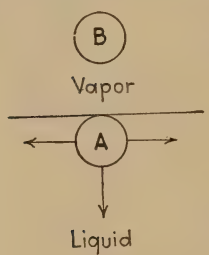

FIG. 3.

A molecule B of the vapor has a still higher potential energy with reference to the interior of the liquid, but the latent heat of vaporization decreases as the temperature rises.

Work and Energy of Surface Cohesion

The relationship between surface energy and cohesion may be exhibited in a simple way by the consideration of a liquid bar of unit cross-section (Fig. 4). If the bar is pulled apart along the plane D, all of the work done against the cohesive forces is utilized in the formation of the two unit surfaces at the plane of rupture, or

$$W_c = 2\gamma$$

Thus, the work done against the cohesive forces is equal numerically to twice the free surface energy, or, in the case of water at 20°C., to 145.6 ergs. While this does not give the value of the force of cohesion, some idea of the magnitude of this force may be obtained by assuming that the two surfaces exert a constant force of attraction until their separation reaches 10^{-8} cm. Now

$$W = Fr$$

or

$$F_c = \frac{W}{r} = 14{,}560 \times 10^6 \text{ dynes} = 14{,}400 \text{ atmospheres}$$

FIG. 4.—Liquid bar of unit cross-section.

This calculation could be made more exactly if the functional relations between F and r were known, since, if the lower end of the bar of liquid (Fig. 4) consists of one liquid and the upper part of another, with an interface at D, the work of separation (W_A) is utilized in producing a unit surface of the liquid 1, and another unit surface of the liquid 2, but it is aided by the energy set free when unit area of the interface 1, 2 disappears, thus

$$W_A = \gamma_1 + \gamma_2 - \gamma_{1,2}$$

which is the well-known equation of Dupré. The total energy

of adhesion is given by a simple modification of this equation, as given by the writer:

$$E_A = (\gamma_1 + l_1) + (\gamma_2 + l_2) - (\gamma_{1,2} + l_{1,2})$$
$$= u_1 + u_2 - u_{1,2}$$

The value of the work of adhesion (W_A) is highly dependent upon the chemical nature of the two liquids. Thus, if water is one of the liquids, the values of W_A are relatively high when the other liquid is an alcohol or an acid, and low when it is a hydrocarbon or a similar compound, as was found by Hardy in 1913.

Monomolecular Films on the Surface of Liquids

That drops of certain liquids spread themselves out into a film one molecule thick was pointed out by Lord Rayleigh[6] in 1899, and more definitely by Devaux,[7] who began his researches on films in 1903. This idea has been applied so extensively in connection with the theory that molecules in surfaces are oriented, that the experimental development of the work on films will be treated in connection with the orientation theory.

The Orientation Theory of Surface Structure

Almost all solid materials possess an internal molecular architecture or structure, which consists of an orderly and symmetrical arrangement of its molecules. This structure was first made apparent by the symmetrical distribution and orientation of the surfaces upon crystals. The interior symmetry of arrangement was later made evident through the effects of crystals upon x-rays as revealed by the fundamental work of Laue.

The passage of x-rays or of ordinary light through ordinary liquids gives no such evidence of any internal structure, though a few specific substances are known to exhibit a certain crystalline structure when in the liquid state. These are known as liquid crystals.

The most fundamental characteristic of a surface is the unlikeness of its two sides and the resultant dissymmetry of the molecular forces involved. If the molecules in the surface are not entirely symmetrical, this lack of balance in the forces must result

in their orientation to a smaller or a greater degree. Since, however, the heat motion of the molecules is very great at ordinary temperatures, it might well be that the orientation would be thus so greatly reduced as to produce no noticeable effect upon ordinary surface phenomena. Thus, not only are the molecules in the surface of water vibrating with extreme rapidity, but their orientation is also disturbed by the escape of about 7×10^{21} molecules from each square centimeter of surface every second (at 20°C.). Not only is this the case, but if the water and its vapor are in equilibrium, molecules to the same number jump back into the surface in the same minute interval of time.* It is thus seen that the idea that there are forces which would produce orientation in a static system is not sufficient to demonstrate that such orientation has an appreciable magnitude. For such a demonstration, definite experimental evidence is necessary.

The idea that the molecules in surfaces are orientated was presented in a remarkably clear way by Hardy in 1912 and 1913, and this idea was developed into a definite and experimentally founded theory by Harkins and by Langmuir independently. The principal lines of evidence presented by these two latter workers were based upon quite different phenomena, although there were naturally many points of similarity, since both investigators had the benefit of Hardy's fundamental suggestions.

The two following quotations, cited from two papers by Hardy, include all that he wrote at that time upon the topic of molecular orientation.

* Since there are about 10^{15} molecules of water in 1 sq. cm. of surface, this means, if we consider the area covered by one molecule, that 7,000,000 times during 1 second the molecule in this area at the instant would jump out into the vapor, and (also on the average) a molecule would fall from the vapor upon this area 7,000,000 times. Since there would also be an enormous number of exchanges between the surface of the liquid and the molecular layer just below, it will be seen that the surface is in anything but a static condition. Thus, if there is to be any appreciable degree of orientation of the molecules on the average, the time of orientation should fall considerably below $\frac{1}{20{,}000{,}000}$ second. Since the data on surface energy indicate a marked degree of orientation in most liquids at this fraction of their critical temperature (0.437), it would seem that the time of orientation is of the order of $\frac{1}{100{,}000{,}000}$ second or less, which seems entirely plausible when the rapidity of rotation of such a system is considered.

The corpuscular theory of matter traces all material forces to the attraction or repulsion of foci of strain of two opposite types. All systems of these foci which have been considered would possess an unsymmetrical stray field—equipotential surfaces would not be disposed about the system in concentric shells. If the stray field of a molecule, that is, of a complex of these atomic systems, be unsymmetrical, the surface layer of fluids and solids, which are close-packed states of matter, must differ from the interior mass in the orientation of the axes of the fields with respect to the normal to the surface, and so form a skin on the surface of a pure substance having all the molecules oriented in the same way instead of purely in random ways. The result would be the polarization of the surface, and the surface of two different fluids would attract or repel one another according to the sign of their surfaces. (Hardy, 1912.)

These ideas are even more clearly expressed in the following passage.

If the field of force about a molecule be not symmetrical, that is to say, if the equipotential surfaces do not form spheres about the center of mass, the arrangement of the molecules of a pure fluid must be different at the surface from the purely random distribution which obtains on the average in the interior. The inwardly directed attractive force along the normal to the surface will orientate the molecules there. The surface film must, therefore, have a characteristic molecular architecture, and the condition of minimal potential involves two terms—one relating to the variation in density, the other to the orientation of the fields of force. (Hardy, 1913.)

While it is not to be expected that the surfaces of two fluids will in any case repel each other unless the surfaces are charged in addition to the polarization produced by orientation, it is seen that in these paragraphs Hardy states the idea of orientation quite definitely, and in the latter paragraph calls attention to the important principle of the minimum potential.

This principle was also used in Langmuir's important contributions to this subject. His initial ideas upon this subject are presented below in the form of quotations from his first paper on orientation.[11]

1. According to this theory, the group molecules of organic liquids arrange themselves in the surface layer in such a way that their active portions are drawn inwards, leaving the least active portion of the molecule to form the surface layer.

2. Surface tension (or surface energy) is thus a measure of the potential energy of the electromagnetic stray field which extends out from the surface layer of atoms. The molecules in the surface layer of the liquid arrange themselves so that this stray field is a minimum.

3. The surface energy of a liquid is thus not a property of the group molecules, but depends only on the least active portions of the molecules and on the manner in which these are able to arrange themselves in the surface layer.

4. In liquid hydrocarbons of the paraffin series, the molecules arrange themselves so that the methyl groups (CH_3) at the ends of the hydrocarbon chains form the surface layer. The surface layer is thus the same, no matter how long the hydrocarbon chain may be. As a matter of fact, the surface energy of all these many different substances, from hexane to molten paraffin, have substantially the same surface energy—namely, 46 to 48 ergs per square centimeter, although the molecular weights differ very greatly.

5. If, now, we consider the alcohols, such as CH_3OH, C_2H_5OH, etc., we find that their surface energies are practically identical with those of the hydrocarbons. The reason for this is that the surface layer in both cases consists of CH_3 groups.

6. With such substances as CH_3NO_2, CH_3I, we find that the surface energy is much greater than that of the hydrocarbons. This is due to the fact that the volume of the I or the NO_2 is so great that the surface cannot be completely covered by the CH_3 radicals. The forcing apart of these groups increases the surface energy.

7. In benzol itself, the group molecules arrange themselves so that the benzol rings lie flat on the surface, since the flat sides of these rings are the less active portions of the molecules. The surface energy of benzol is about 65 ergs per square centimeter.

8. If, now, an active group, such as OH, is substituted for one of the hydrogens in the benzol (forming phenol or carbolic acid), this group is drawn into the body of the liquid, tilting the benzol ring up on edge and raising the surface energy to about 75 ergs per square centimeter, which corresponds to the activity of the perimeter of the benzol ring. Thus, any active group strong enough to tilt the ring up on edge raises the surface energy to about 75. Two active groups side by side (ortho position) have no greater effect than one. But two active groups opposite one another (para position) cannot both go wholly below the surface, so that the surface energy then becomes abnormally large (about 85 in the case of paranitrophenol). The substitution of methyl or ethyl groups in the benzol ring lowers the surface energy, except where an active group in an adjacent position draws these groups below the surface.

9. Some of the best evidence in support of the new theory is derived from experiments on thin films of oil on water or mercury. Oleic acid on water forms a film one molecule deep, in which the hydrocarbon chains stand vertically on the water surface with the COOH groups in contact with the water.

10. Acetic acid is readily soluble in water because the COOH group has a strong secondary valence by which it combines with water. Oleic acid is not soluble because the affinity of the hydrocarbon chains for water is less than their affinity for each other. When oleic acid is placed on water, the acid spreads upon the water, because by so doing the COOH can dissolve in the water without separating the hydrocarbon chains from each other.

11. When the surface on which the acid spreads is sufficiently large, the double bond in the hydrocarbon chain is also drawn down onto the water surface, so that the area occupied is much greater than in the case of the saturated fatty acids.

12. Oils which do not contain active groups, as, for example, pure paraffin oil, do not spread upon the surface of water.

13. The measurement of the area of water or mercury which can be completely covered by a given amount of a substance affords an accurate method of determining the shapes of group molecules. Thus it is found that the molecules of stearic acid on a surface of water have a length of about 23×10^{-8} cm. and cover an area of 24×10^{-16} sq. cm. These measurements prove that the molecules are not spherical, but are much elongated.

An independent development of the orientation theory by Harkins and his associates arose from considerations presented for many years in the lectures of Prof. Julius Stieglitz at the University of Chicago. In an application of the principle "like dissolves like," he emphasized that the carboxyl group of an organic acid gives the acid its solubility in water, while the hydrocarbon chain contributes to its solubility in an organic phase. The writer had been working upon a two-phase system consisting of water and benzol, and it occurred to him that *any butyric acid dissolved in the two phases should, when equilibrium is attained, reach by far its highest concentration at the interface, since there the hydrocarbon group could dissolve in the organic phase, and the carboxyl group in the water.*

While the primary attention of the work in the Chicago laboratory has been given to orientation at interfaces, it was natural that the subject of films of oil on water should also be considered.

Thus, in considering the spreading of oleic acid on water, the writer expressed the fundamental idea "*COOH of acid down because both acid and H_2O associated and polar*," as is shown by Fig. 5, which reproduces a section from the lecture notes*

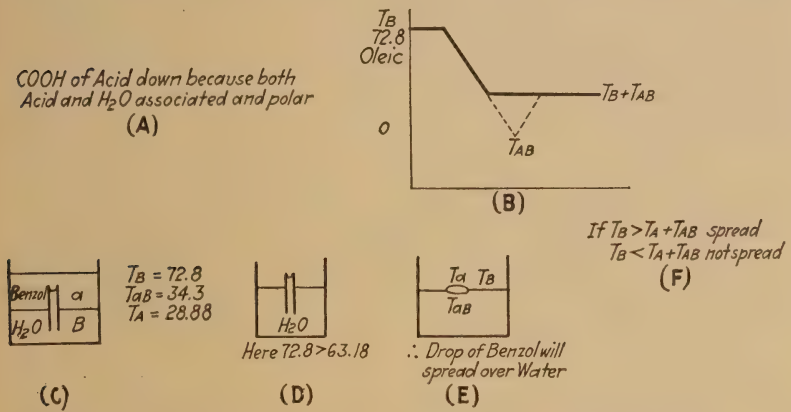

FIG. 5.—A reproduction of notes showing the essential basis of (1) the theory of the orientation of molecules in surfaces, and (2) the principle involved in the spreading of one liquid over the surface of another. (*A*) which states "COOH of acid down because both acid and water associated and polar" is a brief statement of the present theory of orientation. (*B*) illustrates the lowering of the surface tension of water by a film of oriented molecules of oleic acid. (*C*) exhibits the rise of water in a capillary tube covered above by a benzol phase. (*D*) illustrates the same when the upper phase is water vapor, or vapor and air. (*E*) represents a drop of oil which does not spread on water. (*F*) gives the principle of the Neumann triangle, and shows that according to this principle benzol will spread on water, even although it contains no very polar group (hexane also spreads). The notes were taken by George L. Clark from a lecture by the writer as delivered in March, 1914. They represent portions selected from a single page of the note-book.

of George L. Clark, taken in March, 1914. This is the earliest record to give the actual orientation of the molecules in any surface.

Definite evidence that, notwithstanding the heat motion of the molecules, there is an actual mean orientation of the molecules at an interface or a surface was obtained by Harkins, Brown and Davies[12] by a comparison of the work necessary to pull apart a unit bar of a pure liquid W_c—and that used in separating a unit

* These notes state that benzol spreads on water, a fact noted earlier by Hardy. Attention is called to this point, since certain later writers have claimed that benzol does not spread.

bar with two unlike ends just at the interface between the two liquids W_A. Molecules of the type of those of the paraffins may be designated as slightly polar or *homopolar*, while groups of the nature of COOH, etc., may be styled *polar*. A molecule such as that of butyric or lauric acid may be designated, therefore, as polar-homopolar. Such molecules have been represented in this laboratory for many years by the symbol ⌶, in which the upper rectangular part represents the homopolar hydrocarbon chain,

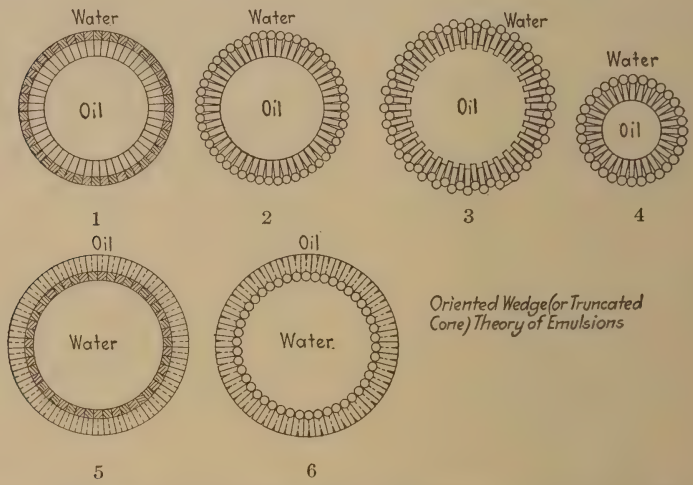

FIG. 6.—Molecules with ends weighted toward water. (*Drawing by Ernest B. Keith*).

and the lower circle, the polar group. In the form of a model, the upper part is a cylinder made of wood, while the lower part, which designates the polar group, is made of iron. Such models may easily be so constructed that they float upright upon the surface of a body of water, with the tops of the wooden cylinders projecting above the surface of the water. A crowded assemblage of such models represents very well the general configuration of a layer of an organic alcohol or acid upon the surface of water, except that the models are much less flexible than the molecules, and motion corresponding to the molecular motion is absent. Figure 6, which will be referred to later in connection with the subject of emulsions, gives a highly conventionalized set of drawings to illustrate the behavior of models with an end weighted

toward water in the case of drops of oil in water, and of water in oil. In subfigures 1 and 5 the polar group is represented by cross-hatching, and in the other diagrams by circles. It is not to be supposed that the orientation is so perfect as this in an actual case, except at very low temperatures.

Subfigure 6 (Fig. 6) gives also the orientation which results if a drop of a polar-homopolar oil, such as nonylic or butyric acid, is suspended in air. The general principles involved are presented in the following quotation from a paper by Harkins, Davies and Clark:[12]

1. The molecules in the surfaces of liquids seem to be oriented, and in such a way that the least active or least polar groups are oriented toward the vapor phase. The general law for surfaces seems to be as follows: *If we suppose the structure of the surface of a liquid to be at first the same as that of the interior of the liquid, then the actual surface is always formed by the orientation of the least active portion of the molecule toward the vapor phase,* AND AT ANY SURFACE OR INTERFACE THE CHANGE WHICH OCCURS IS SUCH AS TO MAKE THE TRANSITION TO THE ADJACENT PHASE LESS ABRUPT. This last statement expresses a general law, of which the adsorption law is only a special case. If the molecules are monatomic, and symmetrical, then the orientation will consist in a displacement of the electromagnetic fields of the atom. This molecular orientation sets up what is commonly called a "double electrical layer" at the surfaces of liquids and also of solids.

This law, if applied to special cases, indicates for a few pure liquids the following orientation: In water the hydrogen atoms turn toward the vapor phase and the oxygen atoms toward the liquid. With organic paraffin derivatives, the CH_3 groups turn outward, and the more active groups, such as NO_2, CN, COOH, COOM, COOR, NH_2, $NHCH_3$, NCS, COR, CHO, I, OH, or groups which contain N, S, O, I, or double bonds, turn toward the interior of the liquid.

If any of these organic compounds are dissolved in water, their orientation in the water surface is the same as that just given, with the active groups inward.

At interfaces between two pure liquids, the molecules turn so that their *like* parts come together in conformity with the general law. With solutions, the solute molecules orient so that the ends of the molecules toward the liquid A are as much like A as possible, and the ends toward B are as much like B as possible. So at interfaces between organic liquids and water, for example, the organic radical sets toward the organic liquid, and the polar group toward the water.

2. If at an interface the transition from a liquid A to the liquid B is made by a saturated film of solute molecules which we may call A-B, that is, they have one end like A and the other like B, then the free surface energy is greatly reduced. For example, with water and benzene with sodium oleate as the solute, the free energy falls as low as 2 ergs per square centimeter.

3. If the solvent is polar, such as water, then solutes will, in general, be positively adsorbed in the surface if they are less polar than water, and the least polar end of the molecule will be turned outward. Solutes more polar than water are negatively adsorbed.

4. The stability of emulsoid particles seems to be brought about by orientation of molecules at the interface with the medium of dispersion. The best emulsifying agents, for example, have very long molecules, with a polar or active group at one end of the molecule. For the emulsoid particle to be stable, the molecules which make the transition from the interior of the drop to the dispersion medium, or the molecules of the "film," should fit the curvature of the drop (Fig. 6).

From this standpoint the surface tension of very small drops is a function of the curvature of the surface.

Definite evidence in support of the general principle of orientation, as expressed in paragaph 1 above, is contained in the data (Harkins, Brown and Davies) for the work done in pulling apart a liquid bar of unit cross-section (Fig. 4). Water is a highly polar compound, and it is found that the work W_A required to pull a unit bar of water into two parts in such a way that two surfaces of unit area are created is 145.8 ergs, a relatively large number as compared to the value given by an organic substance. The work required to accomplish the same result for the slightly polar compound octane is less than a third of that for water, that is, for octane the value is only 43.5 ergs.

It is of interest to determine how the attractive forces between octane and water are affected by the polar nature of the water. The surprising result expressed by the data is that it requires practically no more work to separate octane from water at the interface between the two, than it does to separate octane from octane. Thus, the value of the work of adhesion between octane and water is 43.8 ergs, identical, within the limits of error, with that found for the work of cohesion of octane.

When a bar of octyl alcohol itself is pulled apart, the first effect to be expected is that, where the break is to occur, the molecules

on both sides of the plane of the break should orient themselves so that the break would occur with the least possible expenditure of work. Thus, the molecules should first orient themselves so that the final break can occur between the ends of hydrocarbon chains (Fig. 7). From this point of view, the final amount of work of rupture should be not very different from that given above for octane, or 43.5 ergs. However, two factors should increase this value somewhat: First, at the very beginning of the process which results finally in the separation, a moderate number of hydroxyl groups, which will finally lie on one side of the plane, must be separated from others which will finally lie on the other; and, second, the heat motion of the molecules should detract somewhat from the perfectness of the orientation. When these two factors are taken into consideration, it is seen that the moderate increase in the value of the work to 55.1 ergs is not surprising.

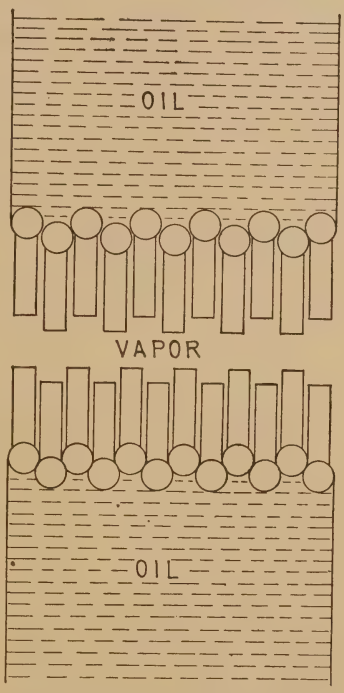

FIG. 7.—Orientation produced when a bar of oleic acid is pulled apart.

When, however, octyl alcohol is pulled away from water, polar hydroxyl groups must be pulled away from polar water, so a high value of the work of adhesion should result from the orientation at such an interface. Corresponding with this it is found that the work of adhesion between octyl alcohol and water (91.8 ergs) is very much greater than the work required to pull octyl alcohol from octyl alcohol (55.1 ergs).

Even more convincing than the above is the fact that the work required to pull alcohol away from water is nearly independent of the size of the molecule, that is, of the fraction of the molecule in the hydrocarbon chain, which would be an entirely unexpected result if orientation is not assumed. Thus, an increase of the

hydrocarbon chain from 1 carbon atom in methyl alcohol to 8 carbon atoms in octyl alcohol reduces the work of adhesion only from 95.5 to 91.8 ergs.

A consideration of the relations at the interface between octyl alcohol and water, from the standpoint of the dimensions found for alcohol molecules in films on water, is of interest. It will be seen later that the number of alcohol molecules per square centimeter is about 3×10^{14}, while it is easily calculated that for symmetrical water molecules the number is about 10×10^{14}. A simple calculation shows that the work necessary to pull the alcohol from water at the interface between the two is about 30×10^{-14} ergs, while in separating water from water it is about 15×10^{-14} ergs, per molecule of water on one side and in a plane. These energy values seem to indicate the probability that at the interface the –OH groups of the alcohol are adjacent to several molecules of water. Also, they suggest that the fact that the work of separation of the alcohol from water (91.8) is smaller than that of water from water (145.8) is not due to the relative smallness of the attractions around the hydroxyl group of the alcohol, but to the relatively small number of such groups as compared with the number in the surface of water, the ratio being only about 1 to 3.3.

The molecule of octane contains 26 atoms. The introduction of a single oxygen atom into this molecule increases the work of surface cohesion in water by only 26 per cent, but it more than doubles the work of adhesion, actually increasing the value by 111 per cent, which is a remarkably high effect for the addition of a single atom per molecule. The values for capryllic acid, with 8 carbon atoms, are almost identical with those for octyl alcohol, since the work of cohesion for capryllic acid is 57.6 ergs, while its work of adhesion toward water is 93.7 ergs per square centimeter. Thus it will be seen that in the case of *non-symmetrical* molecules, such as those of octyl alcohol (C_8H_{17}-OH), capyrllic acid ($C_7H_{15}COOH$), and mercaptan (C_2H_5SH), *the adhesional work W_a is determined by the strongest electromagnetic fields in the molecule, while the tensile-free energy W_c is determined by the weakest fields*, so for unsymmetrical molecules the work of adhesion is relatively high, and the work of cohesion low. In the case of entirely symmetrical molecules there could be no

orientation, though a molecule which is symmetrical in the gaseous state may be expected to become less symmetrical when placed in the non-uniform electrical field at the surface of a liquid. *An increase in symmetry, without a change in the composition of the molecule, is found to increase the work of cohesion, and to decrease the work of adhesion toward water, which is exactly in accord with the hypothesis that the molecules in surfaces are oriented*, since an increase of symmetry not only reduces the extent of the orientation, but it also decreases the effect of such an orientation upon the energy values. Thus it is only when an organic molecule is moderately symmetrical with respect to the electromagnetic field (largely electrical) which it produces that the work of cohesion can become greater than that of adhesion.

It is thus found that the value of $W_A - W_C$, which will be designated as S, is dependent upon lack of molecular symmetry for its high positive values, and upon the presence of such symmetry for its high negative values. For the highly unsymmetrical alcohols, S is about 50, while for the symmetrical acetylene tetrabromide it is -5.7, and for methylene iodide (CH_2I_2) it is -26.5. It will be shown later that S is an important function in connection with spreading, so it may be called the *spreading coefficient*. In general, liquids will spread when S is positive, and will not spread when S is negative.

Figure 8 gives the adhesional work for a number of different liquids. Let us consider carbon disulfide and ethyl mercaptan. The cohesional work in the former is much higher, 62.8 instead of 43.6, yet the attraction between water and carbon disulfide (adhesional work = 55.8) is much less than that between water and mercaptan (68.5).

The former is a symmetrical molecule, and the latter is unsymmetrical. The hydrosulfide group is evidently more polar than the divalent sulfur atom, but when the mercaptan lies in contact with the water, most of the hydrosulfide groups are turned toward the water, and when they are pulled from it, the polarity of the group is evident in the high value of the adhesional work. The = S group, not being so polar, gives a considerably smaller value, which is 12.7 ergs less. However, the attraction between the sulfur of carbon disulfide and water, and also that between the sulfur in the different molecules of the carbon disulfide itself, is

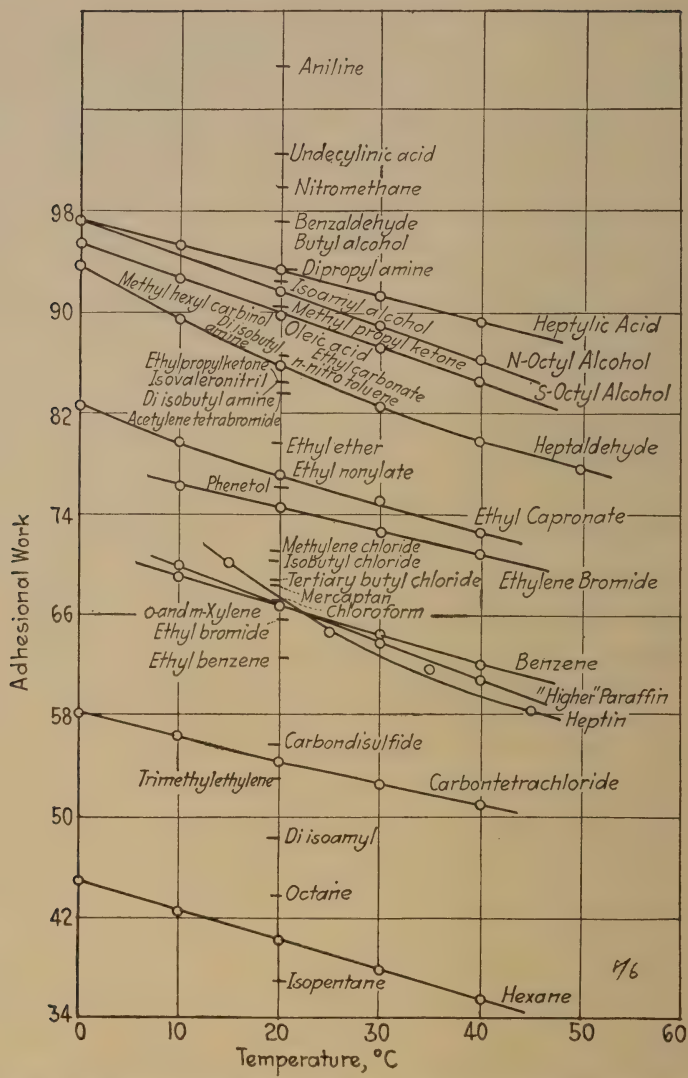

FIG. 8.—Adhesional work, ergs per sq. cm., between organic liquids and water. (The names of the substances represented by the curves are given at the right while the names given in the middle of the diagram represent substances for which the values are given at 20° only.) It will be seen that the substances with symmetrical molecules are near the bottom, and those with unsymmetrical molecules near the top of the illustration.

much greater than the attraction between hydrocarbon groups such as C_2H_5—. Now when a bar of carbon disulfide is pulled apart to make two surfaces, sulfur must be pulled away from sulfur, so the cohesional work and also the total cohesional energy are relatively high, the former having a value of 62.76 ergs per square centimeter. However, when mercaptan is pulled apart, sulfur (—SH) does not need to be pulled from sulfur, but the sulfur turns under the surface, and only the hydrocarbon groups have to be pulled apart, so the work of separation is low (only 43.6).

A comparison of the halogen derivatives is also instructive. The cohesional work for carbon tetrachloride, chloroform, and methylene chloride is almost the same (53.32, 54.26, 53.04), but the adhesional work toward water rapidly increases in the order given (56.16, 67.30, 71.0). Here the increasing polarity is not in evidence in the cohesional but is present in the adhesional work, since, when the pure liquids are pulled apart, the increase of cohesional work due to an increase of polarity is counterbalanced by the concomitant increase of dissymmetry, which allows the less polar parts of the molecules to be oriented into the surface. At the interface, however, it is the most polar part which is turned into the interface, so the effects add together instead of subtracting. Also, the adhesional work for isobutyl and tertiary butyl chloride are practically as high as in the case of methylene chloride, since the chlorine is turned toward the water, but the cohesional surface work drops to very low values, 43.88 and 39.18 ergs per square centimeter.

Both carbon tetrachloride and ethylene dibromide give the same value for the cohesional work as for the adhesional work, but, as the number of bromine atoms in the compound increases (acetylene tetrabromide), the cohesional work becomes the higher. These compounds have very symmetrical molecules.

A comparison of isopentene with trimethyl ethylene and of octane with octylene shows that the introduction of a double bond increases the cohesional work very slightly and the adhesional work very greatly, especially in the latter case, where the double bond is at the end of the molecule. These facts are again exactly in accord with the orientation theory. For octane the cohesional work is 43.54, while for octylene it is almost the same,

or 44.66, so the introduction of the double bond has little effect. The value of the adhesional work for octane is practically the same as that for the cohesional work, but the addition of the double bond in octylene raises the value by about 60 per cent.

In a later paper (Harkins and Cheng[13]) it is shown that the total adhesional energy and the total cohesional energy exhibit, in general, exactly the same relations as those given above for the work involved, except that in the former case all of the energy values are greater. Thus, the addition of 1 oxygen atom to the 26 atoms already present in octane to form octyl alcohol increases the cohesional energy by only 2 per cent, but the adhesional energy by 65 per cent. The cohesional energy of ethylene dibromide is, on account of the symmetry of the molecule, much greater than that of the isomeric but unsymmetrical ethylidene dibromide.

The general effect of double bonds near the end of the molecule is to increase the adhesional, but not the cohesional, work. The double bonds in benzol are distributed with such symmetry that they increase both the cohesional and the adhesional work.

Orientation of Molecules in Surfaces as Shown by the Total Surface Energy and the Heat of Vaporization

Remarkable evidence for the orientation of molecules in surfaces was obtained several years later (Harkins and Roberts,[14] 1921) by considering the average amount of energy necessary to raise a molecule from the interior of a liquid into the surface e, with that necessary to cause it to jump out from the surface j, the energy of thermal emission. The sum of these two equals the heat of vaporization λ, or $e + j = \lambda$.

It is obvious that with unsymmetrical (polar-homopolar) molecules, represented by the symbol ⫿, all that has to be done in getting the molecule into the surface is, according to the orientation theory, to lift its (electromagnetically) *light end* into the surface, while, when the molecule jumps out from the surface, the heavy end has to be lifted, so e is small as compared with j, or with λ. However, with a symmetrical molecule there is no (electromagnetically) relatively light end, so e is much larger as compared with j or λ. Thus, if we plot the

ratio $\frac{e}{\lambda}$, the orientation theory tells us that the curves should lie higher and higher as the molecules become more symmetrical. Remarkably in accord with this prediction, Fig. 9 shows that this

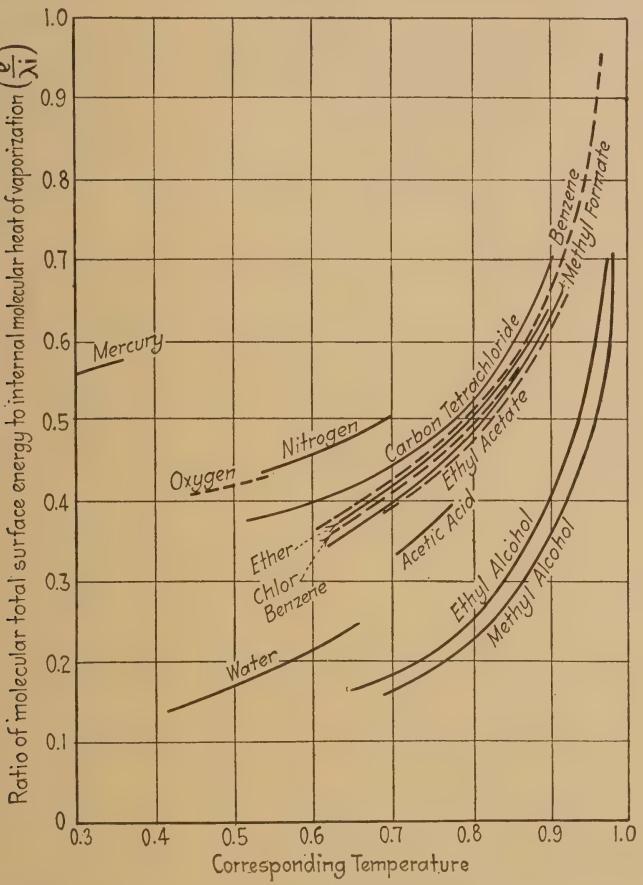

FIG. 9.—The curves show that the ratio $\frac{e}{\lambda}$ of the surface energy (e) to the heat of vaporization (λ) increases as the symmetry of the molecule increases, as corresponds with the theory that the molecules in surfaces are oriented with the electromagnetically "lightest" end up.

is exactly the case, for the most unsymmetrical molecules, those of ethyl and methyl alcohol, lie by far the lowest, while symmetrical molecules, such as nitrogen and oxygen, lie very

much higher in the plot, with mercury, which is monatomic, the highest. Furthermore, the curve for the highly symmetrical CCl_4 lies higher than for any of the other organic substances, and it will be seen that the height of the curve for any organic substance is in complete accord with its degree of symmetry.

It is of interest to note that the value of the surface energy becomes a larger fraction of the (internal) energy of vaporization as the corresponding temperature increases. The shape of the curves seems to indicate that at the critical temperature the ratio becomes 1, or the total surface energy is equal to the heat of vaporization, that is, a molecule which is in the surface is already vaporized.

Orientation and Monomolecular Films

When a small amount of oil, of the general nature of olive oil, is put upon the surface of water, the surface tension of the water is not affected, provided the area is great enough. The oil spreads out until a definite area has been covered, and, in general, shows no tendency to spread further. In 1891 Miss A. Pockels[5] showed that, as the area of the surface is decreased by means of movable barriers, a moderately sharp limit is reached at which, upon further decrease in area, the surface tension begins to decrease rapidly. These experiments were repeated by Lord Rayleigh,[6] who determined the surface tension for films of different mean thicknesses. His results for films of castor oil are shown in Fig. 10, which indicates that the minimum thickness of the film which affects the surface tension of water is 13×10^{-8} cm., while for olive oil he found it to be 10×10^{-8} cm. Since an ordinary atom has a diameter of the order of 2×10^{-8} cm., these films have a thickness of about 5 ordinary atoms, but it will be found that the atoms of carbon are spaced more closely than this. Rayleigh (1899) came to the following conclusion: "We conclude that the first drop in tension corresponds to a *complete layer one molecule thick*, and that the diameter of a molecule of oil is about 1×10^{-7} cm."

However, he considered that the film thickened, until at the point C the layer was 2 molecules thick. Devaux[7] studied thin oil films much more extensively. He says: "We know, therefore, that a film of oil at its maximum extension is formed of only *a single*

layer of molecules." He considers that the lowering of surface tension between *B* and *C*, Fig. 10, is caused by a closer packing in the monomolecular film, which is the present view. These researches established the existence of a two-dimensional region of matter in a novel way, although the ordinary surface energy relations of liquids also indicate the existence of a surface region which has different characteristics from the interior of the liquid phase.

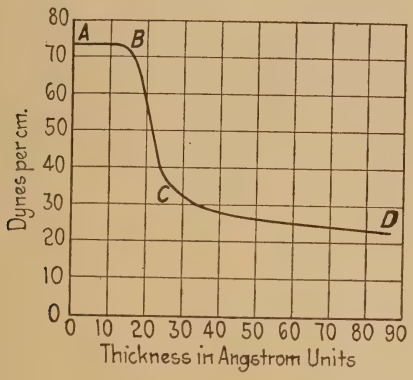

FIG. 10.—Oil films on water. Variation of surface tension with thickness. (*Rayleigh*).

In the work of Miss Pockels,[5] and of Rayleigh[6] and Devaux,[7] a tray of the nature of a photographic tray was used to contain the water. The surface was purified by sweeping with strips of paper or of glass, and the film was confined by barriers of the same materials. Barriers of glass have the advantage that their weight holds them in place, and their use is simple if the surface of the water is given the shape of a great convex meniscus rising above the sides of the trough. Lord Rayleigh determined the tension of the surface by Wilhelmy's method, that is, by measuring the pull upon a knife blade suspended from a balance in such a way that only the lower edge of the blade touches the film. Langmuir[15] introduced an ingenious modification of this method, since he placed the blade in a horizontal position, making it so thin that it would float, and used it in place of the movable barrier at one end of the film. The float was suspended from a balance in order to measure the force of displacement. Since one side of the

float *A* is kept in contact with a pure water surface, and the other side with the oil film, the balance determines the difference between the surface tension of water and that of the film, which is sometimes designated as the force of compression. The method gives the same results as that used by Rayleigh, but the accuracy is increased, since the uncertainty as to the angle of contact of the film with the blade is removed.

The orientation theory indicates that the molecules of the oil would be oriented in such a way that the groups most strongly attracted by the water turn toward the aqueous phase. From chemical evidence Langmuir concludes that these are the polar groups, and this is proved even more directly by the direct measurements by Harkins and his collaborators of the energy values involved, in particular the work of adhesion.

By a combination of the ideas of a monomolecular film and that of orientation with the knowledge of the number of molecules in a gram molecule, Langmuir[15] was able to determine the mean dimensions of the spaces occupied by the molecules in the film, upon the basis of a simple assumption. This was that the density of the oil in the film is the same as that of the same oil in bulk. While it seems certain that this is not strictly true, the method seems to be the best thus far used for the determination of the dimensions of non-spherical molecules. The interesting nature of the results obtained is demonstrated by the following table.

TABLE II

Substance	Formula	Cross-section *A.U.*^{2}	$\sqrt{\text{Cross-section}}$	Length	Length per cation
Palmitic acid.....	$C_{15}H_{31}COOH$	21	4.6	24.0	1.50
Stearic acid.....	$C_{17}H_{35}COOH$	22	4.7	25.0	1.39
Cerotic acid.....	$C_{25}H_{51}COOH$	25	5.0	31.0	1.20
Tristearin.....	$(C_{18}H_{35}O_2)_3C_3H_5$	66	8.1	25.0	1.02
Oleic acid*.....	$C_{17}H_{33}COOH$	46	6.8	11.2	0.62
Myrieyl alcohol.....	$C_{30}H_{61}OH$	27	5.2	41.0	1.37

* The values for this acid are incorrect.

It is apparent that the mean area per molecule does not increase very rapidly with the length of the chain in a normal acid, but is

greatly increased as the number of chains in the molecule increases. These results are in complete agreement with the theory of molecular orientation. The value given above for oleic acid is approximately twice that given by later work in the case of a condensed film, and is apparently due to the appearance of what is designated as an expanded film.

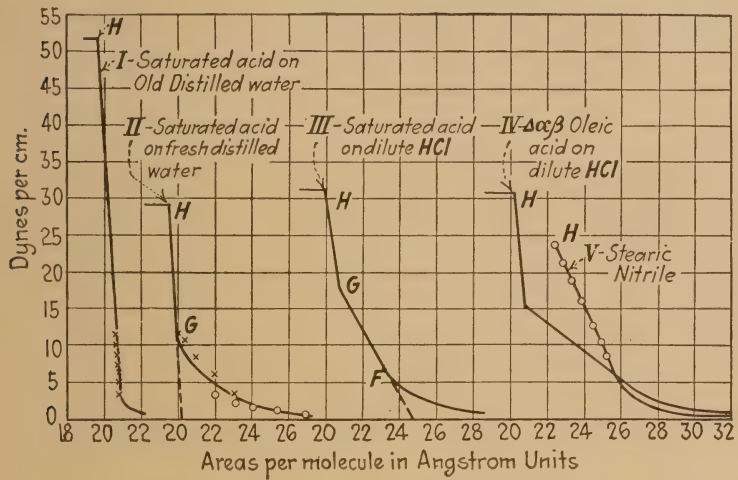

FIG. 11.—Force of compression for films of oil.

The investigation of thin films on water has recently been extended in a series of measurements by N. K. Adam,[16] who introduced refinements in the experimental methods, and exercised great care in the determinations. (Highly accurate measurements of this type have been made also by Harkins and Morgan). Figure 11 presents a few of his results upon the areas per molecule with films of palmitic acid, $\alpha\beta$ oleic acid, and stearic nitrile, at different compressions. Since the compression is merely the surface tension of pure water minus that of the film on water, it is seen that the base of this figure represents, at 20°, a surface tension of 72.8 dynes per centimeter. When the compression rises to 54 dynes per centimeter before it collapses or buckles, as occurs at *I*, *H* with saturated acid on old distilled water, this indicates that the surface tension of the oil film has been reduced to 18.8 before the collapse occurs upon further compression. A collapse or buckling seems

to be due to a heaping up of the molecules, commonly along lines nearly parallel to the barrier, but actually with the approximate form of the arcs of circles. These curves are all obtained by decreasing the area of the film by moving a barrier of glass, which lies on the top edges of the tray, closer and closer to the floating barrier, which is attached to the beam of the balance, and thus measures the force of compression. Adam considers that an extrapolation of the line *HG* to the base of the figure, as in curves I, II, or III, gives the area of the hydrocarbon chains, while an

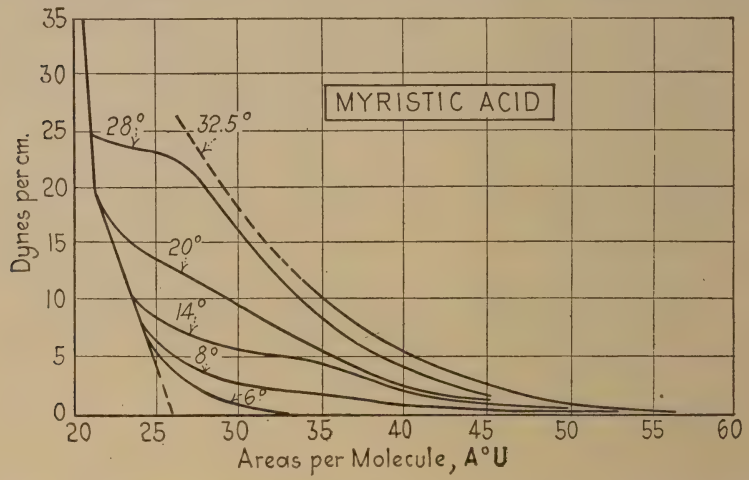

FIG. 12.—Expanded films of myristic acid at 3.5° and 28° on 0.1 N HCl, the remainder on 0.01 N HCl.

extrapolation of the straight line *GF* in curve III gives the area occupied by the head of the molecule, that is, of the carboxyl group, supposed to be in contact with the water. (Films such as those illustrated by curves I or II are considered as "condensed films.")

Earlier investigators had found that condensed films may have the characteristics of a solid or of a liquid. The two may be distinguished by dropping an extremely fine and light wire upon the surface. Gentle blowing is followed by a free movement of such an object if the surface is of the "liquid," but not if of the "solid," type. Labrouste[9] showed that films not only "melt," but they also evaporate in two dimensions. That is, a rise of

temperature causes the molecules to move in the two-dimensional surface in a manner analogous to that in gases, provided the two-dimensional pressure, known as the "*compression*," is kept sufficiently low. Figure 12 gives Adam's results upon the "gaseous" or expanded films obtained with myristic acid. At 3.5° the film does not become expanded at any compression given. It will be seen that each expanded film is transformed into a condensed state at a sufficiently high compression. At

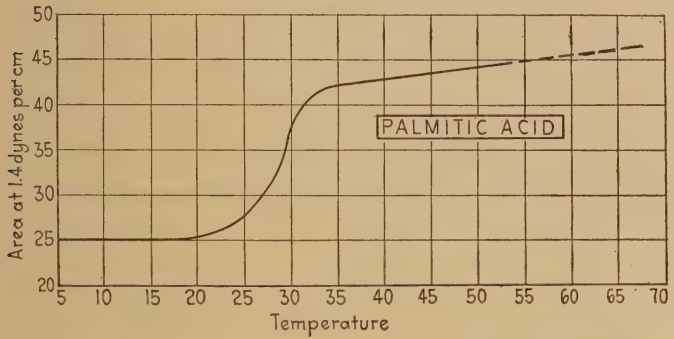

FIG. 13.—Transition from condensed films at lower temperatures to expanded films at higher temperatures. A two dimensional vaporization. Areas taken at low compression (1.4 dynes per cm.).

20° this corresponds to about 18, and at 28° to about 25 dynes per centimeter. Figure 13 represents the data from an experiment in which a film of palmitic acid was kept at low compression, 1.4 dynes per centimeter, and heated from 0 to over 50°. It will be seen that an increase of temperature produces no perceptible increase of area for the condensed film, a considerable increase in area in the expanded film, and a much more rapid increase during the transition. This is in accord with the relations found in the volume expansion of a liquid, of a gas, and during the transition from liquid to gas.

FILMS AND THE SPREADING OF LIQUIDS ON SURFACES

The spreading of a liquid as a film upon the surface of a solid or another liquid is a phenomenon which is of importance not only in nature, but also in connection with many technical processes. Thus, it is difficult for oil to penetrate sand which is

already impregnated with oil, and for water to penetrate sand wet by oil. Also a fundamental characteristic of a good lubricant is that it must spread over the solid surfaces to be lubricated and adhere well to them.

Four different expressions of the criterion of spreading are to be found in the literature. Since these are not all in agreement, they cannot all be correct.

1. All liquids spread on a pure surface.

2. A liquid b will spread on a liquid a if $T_a > T_b + T_{ab}$, where T_{ab} represents the interfacial tension between the two liquids, and T_a and T_b the respective surface tensions. The condition for non-spreading is $T_a < T_b + T_{ab}$.

3. Liquids whose molecules are polar, or contain polar groups, spread on water, while those without polar groups do not spread.

4. A liquid will spread if its work of surface cohesion W_C is less, and will not spread if its work of surface cohesion is greater, than its work of adhesion W_A with respect to the surface of the liquid or solid upon which the spreading is to occur. The *spreading coefficient*, which under the conditions hereafter specified gives a measure of the tendency to spread, is defined as

$$S = W_A - W_C$$

Criterion 4, developed by Harkins and Feldman,[17] is justified both from the theoretical and from the experimental standpoint, and will be used as the basis of the discussion of this subject. Criterion 2, which is obtained by an application of the Neumann triangle of forces, corresponds numerically to criterion 4, but does not rest upon a sound theoretical basis. Criteria 1 and 3 are easily shown to be incorrect, although it seems that the latter of these two is of considerable importance in connection with the thickness of the film which is formed. Thus, the presence of a polar group in an organic molecule seems to be essential to spreading out to a monomolecular film upon water, but not for the formation of one which has a greater thickness.

Criterion 4 as given above is easily developed upon the basis of thermodynamics.

When a drop of liquid b is placed upon the surface of another liquid a, spreading may occur. If it does, the surface of the liquid a disappears, while its place is taken by substantially an equal

area of the surface b plus an equal area of the interface ab, provided the surface of b and the interface ab do not lose their identity. If they do, then only one composite surface c takes the place of the surface a.

The equations will first be developed for the case in which the film does not give a composite surface.

The spreading coefficient may be developed by thermodynamic reasoning, provided the former of the two hypotheses of the preceding paragraph is used as a basis. Since only large-scale motion is of importance in spreading, only the *free* surface energies are involved. The free energy decrease S which occurs in spreading is obviously given by the expression

$$S = \gamma_a - (\gamma_b + \gamma_{ab}) \tag{1}$$

where γ_{ab} represents the free energy of the surface or interface, since the right-hand side of this equation gives merely the net amount of free energy which disappears when the spreading occurs. The work of adhesion W_A, or the work necessary to pull apart the 1 sq. cm. of the interface ab, is given by the equation of Dupré as

$$W_A = \gamma_a + \gamma_b - \gamma_{ab} \tag{2}$$

since all that occurs is the disappearance of the surfaces a and b and the appearance of the interface ab. The work of cohesion is that necessary to create inside a liquid an area equal to 2 sq. cm., or, more specifically, to break apart a bar of liquid 1 sq. cm. in area in such a way as to give two surfaces, each 1 sq. cm. in area, and is given as

$$W_C = 2\gamma_b \tag{3}$$

A combination of (1), (2), and (3) gives

$$S = W_A - W_C$$

which exhibits the extremely simple relation that spreading occurs if the adhesion between the two liquids is greater than the cohesion in the liquid which is in the position for spreading, while spreading does not occur if the cohesion is greater than the adhesion. It is obvious that a positive value of the spreading coefficient corresponds to spreading, a negative to non-spreading. It is also evident that because the liquid b spreads upon a, it is not at all a

necessary conclusion that a spreads upon b. Thus the spreading coefficient is given above for the case where a is the liquid the surface of which is already formed. The coefficient for a to spread upon b is $S = \gamma_b - (\gamma_a + \gamma_{ab})$, so a high surface energy for the liquid a acts in favor of spreading when a is the lower liquid, and against spreading when b is the lower liquid. *Corresponding with this, it is found that almost all organic liquids spread upon water, while water spreads upon very few organic liquids.*

Definition of the Term "Film."—A film exists whenever a layer, which has a different composition from the body of the liquid or solid, is present at the boundary surface, provided the area and form of this layer are independent of the gravitational forces acting. Whenever the area and the form of the layer depend upon both the surface and the gravitational forces, a *lens* exists. If the area and the form of the layer are determined primarily by the containing vessel, the phase may be said to be present in *bulk*.

Films may be said to be *non-composite* and *composite*. In a non-composite film the total surface energy is additive, in that it is equal to the value of the interfacial energy when both phases are present in bulk, plus the value of the surface energy which film-forming material possesses when it exists in bulk in equilibrium with the phase upon which the film rests. In a composite film the total surface energy is less than this—so films may be very different in their degree of compositeness.

Since the distinction between a film and a lens, as given in the last paragraph, may not seem to be sufficiently definite, it will be given below in a slightly different form. The layer of liquid at a phase boundary may be considered to constitute a film whenever the gravitational forces which tend to change its form or area are inappreciable in comparison with the surface forces which are active.

Of the 89 values of the spreading coefficient thus far determined, shown in Table III, only two have a numerical value less than 1 erg, which corresponds to a force of 1 dyne per centimeter. It will be seen that when the thickness of the upper layer is as great as 1μ, or 10^{-4} cm., or approximately 1,000 molecules, the layer may still be characterized as a film, since the gravi-

tational force produced is of the order of only 4×10^{-6} dynes in the case of an organic liquid or water. Even when the thickness is 10μ, or 10^{-3}cm., the gravitational effect is only about 0.0005 dynes per centimeter. Abundant evidence has been obtained both in this laboratory and by Langmuir, that the range of molecular forces for appreciable effects is very minute, and less than the distance across ordinary molecules. It is thus probable that such forces are inappreciable at distances of 10×10^{-8} cm. Thus, a film may have a thickness more than a thousand times the range of molecular forces, and so may have complete independence with respect to the upper surface of the film and its interface with the lower liquid.

From this point of view the spreading coefficient should be entirely significant at thicknesses between the upper limit of an order of 1,000 molecules or more, and some lower limit, which probably approaches closely to only a few molecules in thickness.

The use of the spreading coefficient as an index of spreading would be justified if a large number of spreading coefficients could be determined with considerable accuracy, provided the liquids spread when the coefficient is positive, and do not spread when it is negative. Such a justification has been obtained, for it is shown that this is true of the 89 liquids listed in Table III; only one exception is found, and in that case the magnitude of the spreading coefficient is so low that its sign is doubtful.

The coefficients of spreading listed in Table III apply only to the spreading of the pure liquid upon an entirely clean water surface. If the surface of the water is impure, then the surface tension of the water, which occurs as a positive term in the spreading coefficient equation, is lowered, so the coefficient which should be used in this case has a lower value than the one given. Thus, it has in no case been found that a pure liquid with a negative coefficient will spread, but it is often found in rough experiments that a liquid with a positive coefficient will not spread, due to the presence of a slight impurity on the surface of the water. As organic liquids also, even when purified with great care, often differ slightly in their purity, the spreading coefficient relative to water should be determined by the use of a part of the same sample of liquid as was used in the experiment on spreading.

TABLE III.—THE SPREADING COEFFICIENT OF ORGANIC LIQUIDS ON WATER* AT 20°

A. Spreading Liquids

	S or $W_A - W_C$		S or $W_A - W_C$
Ethyl alcohol	50.40	Ethyl capronate	25.64
Methyl alcohol	50.10	Mercaptan	24.86
Propyl alcohol	49.10	Oleic acid	24.62
Dipropylamine	48.60	*Iso*-amyl butyrate	24.61
Butyl alcohol	48.30	Aniline	24.45
Iso-butyl alcohol	48.20	Heptane	22.40
Propionic acid	45.77	Ethyl nonylate	20.88
Butyric acid	45.66	Trimethyl-ethylene	18.85
Ethyl ether	45.50	Methylene chloride	17.97
Acetic acid	45.20	Ethyl bromide	17.44
Acetonitrile	44.40	Benzaldehyde	17.25
Iso-amyl alcohol	44.30	*Iso*-amyl nitrate	14.82
Iso-valeric acid	43.89	Chloroform	13.04
Methyl ketone	42.37	Anisole	11.76
Di-*iso*butyl amine	40.47	Phenetole	10.66
Methylbutyl ketone	37.58	*p*-Cymene	10.10
Sym-octyl alcohol	37.32	*Iso*-pentane	9.44
Heptylic acid	37.12	Benzol	8.94
Methylhexyl carbinol	36.67	*o*-Xylene	6.85
N-octyl alcohol	35.74	Toluene	6.84
Formic acid	35.50	"Higher" paraffin	6.72
Butyronitrile	34.36	*p*-Xylene	6.70
Iso-amyl chloride	33.88	Tetrachloro-ethane	6.44
Ethylpropyl ketone	33.75	*m*-Xylene	6.19
Ethyl carbonate	33.63	Ethyl benzol, mesitylene	5.59
Iso-valeronitrile	32.63	Trichloro-ethylene	5.09
Heptaldehyde	32.22	*o*-Nitrotoluene	4.15
Undecylenic acid (at 25°)	32.02	*m*-Nitrotoluene	4.13
Methylhexyl ketone	31.92	Nitrobenzene	3.76
Ethyl *iso*-valerate	30.71	Di-*iso*-amyl (decane)	3.76
Monochloro-acetone	30.42	Hexane	3.41
Tert-butyl chloride	29.46	Chlorobenzene	2.31
Asym-dichloro-acetone	26.46	β, β'-dichloro-ethyl sulfide	1.62
Iso-butyl chloride	26.43	Pentachloro-ethane	0.67
Nitromethane	26.32	Octane	0.22

B. Liquids Which Form Lenses on Water

Carbon tetrachloride	1.06(?)	Tribromohydrin	−11.06
p-Bromotoluene	− 1.29(30°)	"Stanolax"	−13.44
Ethylene dibromide	− 3.19	Liquid petrolatum, Squibb's	−13.64
Monobromobenzene	− 3.29	α-Monobromo-naphthalene	−13.86
o-Monobromotoluene	− 4.20	Acetylene tetrabromide	−15.64
Perchloro-ethylene	− 6.42	Methylene iodide	−26.46
Carbon disulfide	− 6.94	Diphenyl methane	
Phenyl mustard oil	− 7.68	Diphenyl dichloromethane	
Monoiodobenzene	− 8.74	Tribromo-ethylene	
Bromoform	− 9.58	*p*-Bromotoluene at 30°	− 1.29
α-Monochloro-naphthalene	− 9.74		

* The values of W_C, from which the spreading coefficients were calculated, relate to the pure dry organic liquids, but the latter in spreading become saturated with water, therefore still more exact information in regard to spreading would be given if W_C were determined by the use of liquids saturated with water.

Spreading as Related to the Presence of Polar Groups in the Molecule

The 71 liquids listed in the first section of Table III were found by careful experiment to spread on the surface of pure water. These 71 liquids include hexane, octane, a higher paraffin, benzol, *iso*-pentane, toluene, *p*- and *m*-xylene, decane (di-*iso*-amyl), ethyl benzene, chlorobenzene, *iso*-butyl chloride, *tertiary* butyl chloride, *iso*-amyl chloride—*a sufficient list to prove that the presence of a polar group is not essential for spreading.*

One of the principal effects of the presence of a polar group is to increase the work of adhesion (W_A). Since, when a very polar group, such as —OH, —COOH, —CONH, —CHO, —CN, —$CONH_2$, etc., is present, W_A is very high, the term W_C in the equation $S = W_A - W_C$ is never large enough to give a negative value of the spreading coefficient. Nevertheless, when the work of adhesion toward water is small, the liquid may still spread if W_C is still smaller. Thus, hexane, for which the value of W_A is very small (40.23 ergs), spreads, since W_C is extremely small (36.86), and the value of S is 3.37. The work of cohesion in octyl alcohol is nearly 20 ergs greater, so octyl alcohol is able to spread only because W_A is also greater (by the remarkably great value 51.71) than that for hexane. This illustrates the fact that the extremely great effect of the presence of a polar group in producing spreading is due to the fact that, in general, it increases the work of adhesion toward water very much more than it increases the work of cohesion.

One of the most important factors in determining the magnitude of the spreading coefficient toward water is the dissymmetry of the molecule. In general, the value of the coefficient increases as the electromagnetic field of force around the molecule becomes more unsymmetrical. This is due to the fact that with unsymmetrical molecules the work of adhesion toward water is much greater, in comparison with the work of cohesion, than in the case of symmetrical molecules, since, when the liquid is torn from water, the strongest field must be ruptured, while, when it is separated from itself, only the weakest field is broken.

Non-spreading Liquids

It has been indicated in the preceding paragraph that one of the important factors in producing a non-spreading liquid is that the intensity of the electrical field around the molecule shall be distributed symmetrically in the case of the upper phase.

It will be seen that, as with the paraffins, spreading may be due to a low value, less than 50, of the free energy of attraction toward water (work of adhesion), but in many more instances is brought about when this value is as high (about 75) as if they were esters, which spread to a monomolecular film. *Thus non-spreading is usually due to a high value of the work of cohesion of the substance.*

Non-spreading seems to accompany the presence of the =S or =CS or phenyl groups, or that of chlorine, bromine, or iodine, as substituents in paraffins, in benzol, or in naphthalene, even when the unsubstituted compound spreads easily. When only one chlorine atom is present in a paraffin derivative it seems to be polar and produces the opposite effect, considerably increasing the spreading coefficient, while with several chlorine atoms the coefficient is decreased. Bromine, and especially iodine, are much more effective than chlorine as substituents for producing non-spreading. The above groups are evidently of the type which have a high attraction for themselves without having an especially high attraction for water.

Insolubility as an Accompaniment of Non-spreading

It would seem that the difference between the adhesional work and the cohesional work ($W_A - W_C$) should be important as a factor in determining solubility (though not so important as in the case of spreading), since the solubility of a substance also seems to depend on the difference between the attraction of the solute for the solvent and for itself. However, there is this distinction: In spreading on water it is the most active or polar part of the molecule which is chiefly involved, while the whole molecule takes part in solution. From this standpoint it is to be expected that spreading on water is a more common phenomenon than a considerable solubility in water, since spreading is a solution of only the most active or soluble part of the molecule.

In spreading it is not necessary for the molecules of the solute to penetrate between and push apart those of the solvent, as must be done in solution.

Corresponding with this, it is found that all non-spreading liquids are practically insoluble. Liquids with very high spreading coefficients with reference to water are miscible with it, provided the slightly polar (homopolar) part of the molecule is sufficiently small. Although the value of the coefficient for ether is moderately high (45), it is not miscible with water, since two ethyl groups are present in the molecule. Most liquids whose coefficients have positive values less than 10 are insoluble or only slightly soluble in water.

Effect of Impurities on Spreading

That impurities on the surface prevent spreading has been pointed out by many investigators; that active impurities in a non-spreading liquid may cause it to spread has been shown by Hardy and others. A simple and beautiful experiment illustrates the latter effect. A large lens of "Liquid Petrolatum, Squibb"—presumably any other oil with a high negative coefficient would give similar effects—is formed in the middle of the surface of a sheet of water in a large tray. A drop of oleic acid is then placed upon the center of this lens. After a short period, considerable movement is noticed adjacent to this point and then, very suddenly, the lens is broken up into a great number of fragments which seem to be projected with almost explosive violence toward the edges of the tray. If the oleic acid is mixed with the oil before it is put on the surface, the material separates into a large number of minute drops, separated by a thin film, the drops moving constantly on the surface. The thin film evidently contains a considerable proportion of oleic acid.

The Spreading of Liquids upon the Surface of a Metal

The spreading of liquids upon the surface of a metal is of particular interest in connection with the problem of lubrication and that of flotation. Experiments with mercury[17] show that the spreading coefficient for water (32) is high, and much higher

(from 60 to 137) for all of the 29 organic liquids tested. Thus, all of these liquids, and probably all other organic liquids, should spread upon this metal, and, presumably, upon the surface of other metals. Careful experiments with 23 of these liquids, including water, resulted in spreading in every case, as predicted by the positive value of the spreading coefficient. Water does not spread upon an ordinary surface on mercury on account of the contamination of the surface by various substances, but spreads readily when the mercury is distilled in a vacuum in clean vessels, as was found by Rayleigh.[30] It is of interest to note that the higher alcohols and acids, which spread so readily on water, have specially high spreading coefficients on mercury, while, on the other hand, the presence of bromine or iodine in the molecule, which results in non-spreading with water, gives the greatest tendency to spread upon mercury.

The work necessary to separate an organic liquid from mercury is especially high for iodine, bromine, sulfur, and carboxyl derivatives, which indicates that these groups are oriented toward the surface of the metal.

The Non-spreading of Water on Organic Liquids

The spreading coefficient for the spreading of water on an organic liquid is negative in all known cases, which indicates that water will not spread upon the surface of any organic liquid when the two are mutually insoluble. Corresponding with this, water was found to spread upon the surface of only one of 18 organic liquids tested, and this one was acetone, which is miscible with water. When a small drop of water is placed upon the surface of any organic liquid which will not spread on water, the drop remains upon the surface in a nearly spherical form. If, however, the organic liquid spreads on water, it will be seen that after the water drop is placed upon its surface, the organic liquid spreads as a film over the surface of the drop, and this then sinks if it is heavier than the organic liquid, but floats as a practically spherical drop if it is lighter.

Heat of Adsorption

An important phenomenon in which surface energy relations are involved is the liberation of heat which accompanies adsorp-

tion. This may be illustrated by citing what occurs when lumps of outgassed charcoal are dropped into a liquid, though in this case the heat liberated does not correspond to the formation of a monomolecular film on the surface of a plane solid, so it may be more properly designated as the heat of immersion. One gram of bone charcoal, which had not been outgassed, gave a heat of immersion of 18.5 cal. in water, while the data of Lamb and Coolidge indicate a value of about 35 cal. for the heat of immersion of outgassed coconut-shell charcoal in carbon disulfide.

The heat of immersion of a solid, the surface of which is so nearly plane that its surface energy is essentially equal to that of the same area of a plane surface of the same material, or the heat of adsorption of a liquid on the surface of the solid, may be defined in a corresponding way as the amount of heat liberated ($-Q_a$) when a solid with a surface of this type, and of an area of 1 sq. cm., is immersed in a liquid in such a way as not to increase materially the area of the surface of the liquid. In this process the surface of the solid would disappear, and in its place would appear the same area of interface solid-liquid. The heat liberated ($-Q_a$) would be equal to the total amount of energy given off in the process when carried out isothermally (E_a), and this is equal to the total surface energy of the solid (E_s), minus the total surface energy of the interface (E_i), for 1 sq. cm. of surface. Since the total surface energy is always equal to the free surface energy (γ) plus the latent heat of the surface ($-T\frac{\partial \gamma}{\partial T} = l$), the following equation expresses the value of the heat of adsorption.

$$-Q_a = E_a = E_s - E_i = \gamma_s + l_s - (\gamma_s + l_s) =$$

$$\gamma_s - T\frac{\partial \gamma_s}{\partial T} - \gamma_i + T\frac{\partial \gamma_i}{\partial T} \quad (1)$$

It is obvious that this equation is also valid for the heat of immersion of a liquid, or for the heat of adsorption of one liquid on the surface of another liquid, so in its more general sense the subscript s refers to the phase whose surface is already developed, but later disappears, giving place to an interface of the same area. The heat liberated on the immersion of a solid has always been found to be a positive quantity, which indicates that the total interfacial energy per unit area is always less, so long as

this holds true, than the total surface energy of the solid. That this is not always the correct sign of the effect, at least when only liquids are involved, is shown by the fact that hexane, octane, and carbon tetrachloride have negative heats of immersion in water equal, respectively, to -0.21, -0.21, -0.26 times 10^{-6} cal. per square centimeter at 20°, though the heats of immersion of water in these liquids are all positive, 1.4, 1.34, and 1.05 times 10^{-6} cal. per square centimeter. Even in the case of two liquids, heat is almost always evolved on immersion as the result of the surface energy changes. Thus, for example, the heat of immersion of normal octyl alcohol at 20° in water is 1.28, and of water in octyl alcohol, 2.85, in terms of the units used above.

The heat liberated on adhesion ($-Q_A$), and the total adhesional energy (E_A), are always larger positive (or smaller negative) quantities than those which give the heat liberated on immersion (heat of adsorption), provided the surfaces are plane. The following equation gives the heat of adhesion.

$$-Q_A = E_A = E_s + E_l - E_i = (\gamma_s + l_s) + (\gamma_l + l_l) - (\gamma_i + l_i) \quad (2)$$

These are the same as the heat and energy of approach, since the surfaces of two phases already in existence approach each other and disappear, while an interface, equal in area to that of either surface which disappears, takes their place. The heat of adhesion is 2.6 for water-hexane, 4.0 for water-octyl alcohol, 2.5 for water-carbon tetrachloride, all in 10^{-6} cal. per square centimeter at 20°.

When a liquid spreads over a solid, the surface of the solid disappears, while an interface of the same area appears. If the solid has a plane surface, then a liquid surface of the same area also appears; so, provided the liquid layer is not too thin, the following equation holds

$$-Q_{sp} = E_{sp} = E_s - (E_l + E_i) = \gamma_s + l_s - (\gamma_l + l_l) - (\gamma_i + l_i) = E_A - E_c$$

where E_c represents the energy of surface cohesion of the liquid.

Obviously

$$-Q_a = E_a = E_A - E_l$$

or the heat liberated by the adsorption of a liquid equals the energy of adhesion minus the surface energy of the liquid. Also

$$-Q_a = E_a = E_{sp} + E_l$$

and

$$E_{sp} = E_A - 2E_l$$

The heat of adsorption of a saturated vapor is

$$-Q_g = (\gamma_s + l_s) - (\gamma_i + l_i) + \lambda v = E_s - E_i + \lambda v$$

where $-Q_g$ is the heat of adsorption of enough vapor to form a liquid in bulk covering the solid surface at constant temperature, and λ is the latent heat absorbed in the vaporization of the liquid per unit volume of vapor. It is assumed here that the area of the surface of the liquid formed is negligible in comparison with the area of the interface which is formed.

The heat of adsorption as defined above is thus found to be 3 25 for *iso*-butyl alcohol, 2.60 for *secondary* octyl alcohol, and 3.13 for octane, all in 10^{-6} cal. per square centimeter. The heat of spreading of *n*-octyl alcohol on water is about that of *iso*-butyl alcohol on mercury, but that for octane on water is less than half the similar value for mercury.

Adsorption

The principle of minimal potential finds one of its most fruitful applications in connection with the distribution of a substance between a phase and its surface. The fundamental relations involved were deduced by Gibbs,[4] and are best known in connection with his equation for adsorption. It has been found by Traube[18] and other investigators that many substances, for example, the organic acids, alcohols, and amines, greatly lower the surface tension, and, therefore, the free surface energy of water, and that this lowering increases as the concentration of the solution increases. If a solution of such a *surface active* substance could be prepared at first in such a way that the concentration is the same at the surface as in the interior, then the free energy would be decreased by a movement of solute into the surface, that is, by a decrease in the concentration of the interior and an increase in the concentration at the surface.

The change would proceed until the free energy of the solute in the interior is lowered and that on the surface is increased to a like value in both. An increase in the concentration of the solution increases the osmotic pressure and the free energy, or it may be said that it increases the *escaping tendency* of the solute. This brings about a corresponding increase in the escaping tendency of the substances in the film. Over a considerable range of concentration in the solution, the concentration in the film is apparently constant, but this is only in the range in which the film consists of a monomolecular layer of the adsorbed substance. Here the concentration of the water is so low that it may vary greatly, even though the variation is inappreciable in terms of the solute. Also the escaping tendency of the adsorbed substance may be affected by a change in its packing along the surface without any marked difference in surface density. This is analogous to the fact that, while a marked increase in pressure produces a considerable density change in a gas, the change in the density of a liquid may be inappreciable if only rough methods are used for the density determinations.

In dealing with adsorption, both phases and phase boundaries are involved, and these may be considered as *regions*.[19] Thus, when we deal with a beaker of water, six regions are involved when the support for the beaker is neglected. These are the regions (1) glass, (2) water, (3) air and water vapor, (4) the interface glass-water, (5) the interface glass-air vapor, and (6) the interface water-air vapor. Thus, for the three phases, there are six regions.

The equation of Gibbs may be developed by a consideration of the dilution or concentration of the solution by means of a piston provided with a semi-permeable membrane, and of the variation in the area of the surface by means of a variable float or barrier. The thermodynamic relations between the energy changes involved give the desired equations when suitably combined. The most complete development of this kind, since it is the only one which deals with the phases on both sides of the interface, was produced by A. C. Lunn[20] at the request of the writer. It is given below. It is based on the laws of thermodynamics and the equation for maximum work considered in connection with osmotic pressure.

Notation: λ = latent heat, μ = adsorption, a = area, γ = surface tension } of film

p,p' = osmotic pressures, l,l' = latent heats, v,v' = volumes, r,r' = dilutions, or reciprocals of concentrations (c,c') } of volume phases

s = entropy

c = thermal capacity of system

M = total mass of solute

q = heat added to system

w = work done by system

ψ = Helmholtz free energy

The first law of thermodynamics may be stated in the form

$$dq = c\,dt + l\,dr + l'\,dr + \lambda da \tag{1}$$

The equation for reversible work is

$$dw = p\,dv + p'\,dv' - \gamma da \tag{2}$$

The negative of the differential of the function of Gibbs, or of the Helmholtz free energy, is defined as

$$\begin{aligned} -d\psi &= d(st) - (dq - dw) \\ &= s\,dt + t\,ds - (dq - \gamma dw) \\ &= s\,dt + dw \qquad (3) \\ &= s\,dt + p\,dv + p'\,dv' - \gamma da \qquad (3b) \end{aligned}$$

The total mass of solute (M) is given by the following equation:

$$M = vc + v'c' + \mu a$$

or

$$\frac{v}{r} + \frac{v'}{r'} = M - \mu a \tag{4}$$

Since r and r' are related at a given temperature, and also p and p', the independent variables may be taken as t, r, v, and a. Then p, p', l, l', λ, μ, and γ will be functions of r and t.

The mass of substance in the phase represented by primed letters is given as follows:

$$m' = v'c' = \frac{v'}{r'} = M - \mu a - \frac{v}{r}$$

so

$$v' = r'\left(M - \mu a - \frac{v}{r}\right) \tag{5}$$

so

$$\begin{aligned} dv' = &\left(\frac{\partial r'}{\partial r}dr + \frac{\partial r'}{\partial t}dt\right)\left(M - \mu a - \frac{v}{r}\right) \\ &-r'\left(a\frac{\partial \mu}{\partial r} - \frac{v}{r^2}\right)dr - r'a\frac{\partial \mu}{\partial t}dt \\ &-\frac{r'}{r}dv - r'\mu da \end{aligned} \tag{6}$$

$$\begin{aligned} -\left[\frac{\partial r'}{\partial t}\left(M - \mu a - \frac{v}{r}\right) - r'a\frac{\partial \mu}{\partial t}\right]dt + \\ \left[\frac{\partial r'}{\partial r}\left(M - \mu a - \frac{v}{r}\right) - r'\left(a\frac{\partial \mu}{\partial r} - \frac{v}{r^2}\right)\right]dr \\ -\frac{r'}{r}dv - r'\,\mu da \end{aligned} \tag{7}$$

Substituting (7) in (3*b*):

$$\begin{aligned} \therefore -d\psi = &\left\{s + p'\left[\frac{\partial r'}{\partial t}\left(M - \mu a - \frac{v}{r}\right) - r'a\frac{\partial \mu}{\partial t}\right)\right\}dt \\ &+ p'\left\{\frac{\partial r'}{\partial r}\left(M - \mu a - \frac{v}{r}\right) - r'\left(a\frac{\partial u}{\partial r} - \frac{v}{r^2}\right)\right\}dr \\ &+\left(p - \frac{p'r'}{r}\right)dv - (\gamma + p'r'\mu)da \end{aligned} \tag{8}$$

In order that this may be an exact differential, the following conditions must be met—(9), (10), (11), (12):

$$\begin{aligned} \frac{\partial}{\partial r}&\left\{s + p'\left[\frac{\partial r'}{\partial t}\left(M - \mu a - \frac{v}{r}\right) - r'a\frac{\partial \mu}{\partial t}\right]\right\} \\ &= \frac{\partial}{\partial t}\left\{p'\left[\frac{\partial r'}{\partial r}\left(M - \mu a - \frac{v}{r}\right) - r'\left(a\frac{\partial \mu}{\partial r} - \frac{v}{r^2}\right)\right]\right\} \end{aligned} \tag{9}$$

$$\frac{\partial}{\partial v}\left\{s + p'\left[\frac{\partial r'}{\partial t}\left(M - \mu a - \frac{v}{r}\right) - r'a\frac{\partial \mu}{\partial t}\right]\right\} = \frac{\partial}{\partial t}\left(p - \frac{p'r'}{r}\right) \tag{10}$$

$$\frac{\partial}{\partial a}\left\{s + p'\left[\frac{\partial r'}{\partial t}\left(M - \mu a - \frac{v}{r}\right) - r'a\frac{\partial \mu}{\partial t}\right]\right\} = -\frac{\partial}{\partial t}(\gamma + p'r'\mu) \tag{11}$$

$$\frac{\partial}{\partial v}\left\{p'\left[\frac{\partial r'}{\partial r}\left(M - \mu a - \frac{v}{r}\right) - r'\left(a\frac{\partial \mu}{\partial r} - \frac{v}{r^2}\right)\right]\right\} = \frac{\partial}{\partial r}\left(p - \frac{p'r'}{r}\right) \quad (12)$$

$$\frac{\partial}{\partial a}\left\{p\left[\frac{\partial r'}{\partial r}\left(M - \mu a - \frac{v}{r}\right) - r'\left(a\frac{\partial \mu}{\partial r} - \frac{v}{r^2}\right)\right]\right\} = -\frac{\partial}{\partial r}\left(\gamma + p'r'\mu\right) \quad (13)$$

$$\frac{\partial}{\partial a}\left(p - \frac{p'r'}{r}\right) = -\frac{\partial}{\partial v}(\gamma + p'r'\mu) \quad (14)$$

(14) is identically satisfied as $0 = 0$.

(10) and (11) give

$$-\frac{\frac{p'\partial r'}{\partial r}}{r} + \frac{p'r'}{r^2} = \frac{\partial p}{\partial r} - \frac{\frac{p'\partial r'}{\partial r}}{r} - \frac{\frac{\partial p'}{\partial r r'}}{r} + \frac{p'r'}{r^2} \quad (15)$$

$$-p'\mu'\frac{\partial r'}{\partial r} - p'r'\frac{\partial \mu}{\partial r} = -\frac{\partial \gamma}{\partial r} - p'r'\frac{\partial \mu}{\partial r} - \frac{\partial p'}{\partial r}r'\mu - p'\mu\frac{\partial r'}{\partial r} \quad (16)$$

or

$$\frac{\partial p}{\partial r} - \frac{\frac{r'\partial p'}{\partial r}}{r} = 0 \quad (15')$$

$$\frac{\partial \gamma}{\partial r} - r'\mu\frac{\partial p'}{\partial r} = 0 \quad (16')$$

$$\therefore \frac{r'\partial p'}{\partial r} = \frac{r\partial p}{\partial r} \quad (17)$$

and

$$\mu = -\frac{\frac{\partial \gamma}{\partial r}}{\frac{r'\partial p'}{\partial r}} = -\frac{\frac{\partial \gamma}{\partial r}}{\frac{r\partial p}{\partial r}} \quad (18)$$

or the adsorption in mols is equal to the concentration of the solution times the rate of increase of the surface tension with the dilution divided by the rate of *decrease* of the osmotic pressure with the dilution.

(17) gives

$$\frac{r'}{r} = \left(\frac{\partial p}{\partial p'}\right)dt = 0 \quad (19)$$

Equation (19) may be written in the form

$$\frac{c}{c'} = \left(\frac{\partial p}{\partial p'}\right)dt = 0$$

or the rate of change of the osmotic pressure in one phase with respect to that in the other, at constant temperature, is equal to the ratio of the respective concentrations.

In the special case where the van't Hoff formula holds:

$$pr = \mathrm{RT} \quad p'r' = \mathrm{RT}$$

$$\therefore \frac{r'}{r} = \frac{p}{p'}; \ \therefore \frac{dp}{dp'} = \frac{p}{p'} \tag{20}$$

isothermally, and $\frac{p'}{p}$ is a function of t; $\therefore$ $\frac{r'}{r}$ is a function of t, which, changing r to $\frac{1}{c}$ gives

$$\mu = -\frac{1}{\mathrm{RT}}\frac{cd\gamma}{dc} = -\frac{1}{\mathrm{RT}}\frac{c'd\gamma}{dc'} = -\frac{1}{\mathrm{RT}}\frac{d\gamma}{d\ln c'} = -\frac{1}{\mathrm{RT}}\frac{d\gamma}{d\ln c} \tag{21}$$

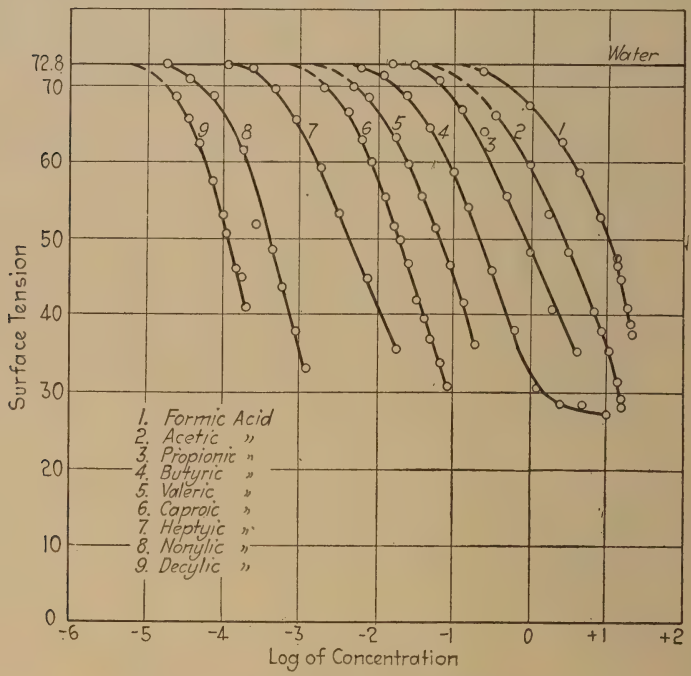

FIG. 14.—Adsorption curves for fatty acids.

The validity of this equation was tested by Donnan and Barker,[21] by bubbling air through a solution of nonylic acid. They found by this direct method that the adsorption was 1.0×10^{-7} g. per square centimeter, while the Gibbs' equation gave 0.6×10^{-6} if the value 2 was assumed for the factor i. The con-

firmation was thus within the limits of error of the experiments and the assumptions.

The surface tensions of solutions of organic acids, alcohols, and other similar substances have been investigated by Traube,[18] Drucker,[22] Whatmough,[20] Szyszkowski,[24] and others. The measurements on the organic acids have been repeated and extended to decylic acid by Harkins, King, and Clark, and their results are given graphically in Fig. 14, which will be used as a basis for the discussion which follows. Curves 5 and 6 are plotted from the

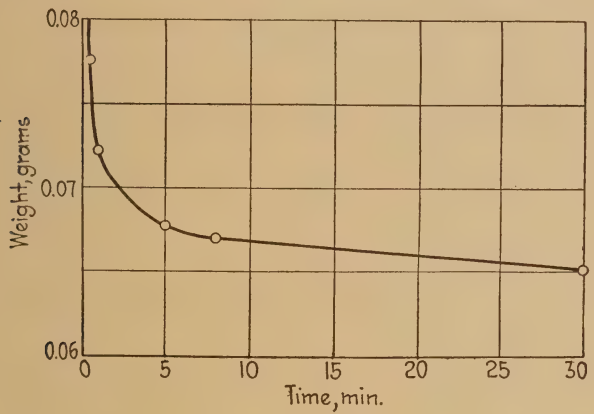

FIG. 15.—Effect of time on the drop weight of decylic acid, 0.00015 N.

data of Drucker, and it will be noted that the curve for capryllic acid, with 8 carbon atoms, is missing. The data were determined by the drop weight method, since the capillary height method proved inaccurate for the higher acids. Figure 15, which was obtained in connection with the experiments, illustrates the fact that adsorption is a process which occupies considerable time, the time to obtain approximate equilibrium increasing with great rapidity with the length of the hydrocarbon chain. Thus, equilibrium was not established with a 0.0015 N solution of decylic acid in the course of half an hour. This makes the determinations tedious, since the drop must be held suspended in saturated vapor for a very long time. The slowness in obtaining equilibrium is due to the fact that a highly concentrated film must be formed, consisting of practically a film of acid, by diffusion

from a solution which contains only 1 molecule of acid in 360,000 molecules of water.

From Milner's result[25] for acetic acid, Langmuir[15] calculates that there are 2.3×10^{14} molecules per square centimeter, or the area occupied per molecule is 43 A.^{2} U., while from Szyszkowski's equation he gets the area 31 A.^{2} U. for the acids with 3, 4, 5, and 6 carbon atoms. These areas are not very different from that (21.6 A.^{2} U.) which he obtained for the higher fatty acids, so he reaches the conclusion that the surface is covered with a monomolecular film of the acid over the region in which the slope of the curves (as in Fig. 12) remains constant over a considerable range of concentration. He considers that the rate at which molecules escape from the liquid phase into the surface is proportional to the concentration of the solution, but the rate at which they return from the surface back to the interior depends upon the number of molecules in the surface, but is also dependent to a very great degree upon the difference in the potential energy of the molecule in the two states.

From Traube's data, Langmuir calculated the areas occupied by a molecule for 24 organic substances. The results for a part of these are listed below.

No. C atoms	Area in A.^{2} U.			
	Normal acid	Iso-acid	Alcohol	Iso-alcohol
1				
2	....	....	32.0	
3	33.8	....	29.1	34.7
4	31.2	31.2	....	27.8
5	....	30.5	....	27.8

For comparison, the results obtained for the normal acids and alcohols by Harkins, King, and Clark are also given. The results for formic and acetic acid are only approximate, since, for the concentrations used, the osmotic pressure is not proportional to the concentration of the solutions. For acids above 10 carbon atoms, the results were obtained from surface films by Adam.

No. C atoms	Area in A.² U.	
	Acids	Alcohols
1	57.0	
2	50.0	
3	39.0	
4	36.0	28
5	(32.0)	
6	(31.0)	
7	34.0	
8	....	34
9	32.0	
10	31.0	
14	25.1	
15	25.1	
18	25.1	
22	25.1	

(Values in parentheses from data by Drucker.)

These results are just the opposite of what would be expected if orientation were absent, since the area per molecule decreases with increase in the size of the molecule. This indicates, as has been pointed out by Langmuir and Adam, that the long chains hold together better than the short ones.

By taking into account the kinetic equilibrium between the surface layer and the interior of the solution, and by the use of an empirical equation of Szyszkowski, Langmuir calculated the decrease in potential energy which occurs when a gram molecule of solute passes from the interior into the surface film. This decrease in potential energy becomes greater and greater as the curves in Fig. 12 shift toward the region of lower concentrations. It will be seen that the shift in the logarithm of the concentration is equal to 0.555 per CH_2 group added. Langmuir calculates that this corresponds to 625 cal., and that

$$\lambda = \lambda_o + 625\ n$$

where λ is the decrease in potential energy, and λ_o is the value given below:

Values of λ_o in Calories per Mol

Tertiary alcohol	950
Primary amine	600
Primary alcohol	575
Ester	470
Monobasic acid	437
Ketone	295
Aldehyde	210
Amide	−510
Dibasic acid or alcohol	−700

The considerations given above give remarkably strong evidence that the molecules in such adsorbed films are oriented.

Equally striking evidence has been obtained in an investigation by Harkins and King,[33] in which different types of interfaces are compared. It was found that the film of constant composition, or the monomolecular film, contains 2.78×10^{14} molecules per square centimeter at the interface between water and vapor, and that between water and benzol there are 2.77×10^{14} molecules. This is extremely remarkable, since it shows that the number of molecules in the film is independent of the nature of the second phase, which would be very difficult to understand upon any other basis than that the number is conditioned by the same closely packed and orderly arrangement of the molecules in both cases.

While the number of molecules in the constant film is the same at the interfaces water-air, and water-benzol, the drop in potential experienced by a molecule when it passes from the water into the surface water-vapor is very much greater than when it goes into the interface water-benzol, that is, the surface of water is a very much more efficient trap for molecules of the polar-homopolar type, designated by the symbol ⌷, than the interface between water and benzol.

This result may be considered from the standpoint of the intermolecular electromagnetic fields involved. Since cohesion depends upon the intensity of these fields, it may be considered that the fields are extremely weak in liquid helium, the liquid of lowest cohesion, and extremely high (interatomic fields) in diamond, in which the cohesion is the highest known.

If two phases, A with the higher and B with the lower intensity of stray field uniting the molecules, could be put in contact in

such a way as to have the field of each perfectly uniform up to a plane phase boundary or interface between them, then the whole drop in intensity between the two phases would occur in a surface of infinitesimal thickness; so, at least by certain methods of mathematical analysis, the free surface energy would be infinite. While this is not an actual case, it suggests the idea that, as the thickness of the transition layer increases, the free surface energy diminishes. *With a given thickness of the surface layer*, the free surface energy increases as the intensity of the stray field in B decreases, so the maximum free surface energy is reached when B is a vacuum, and is nearly realized when it is a dilute vapor or gas.

In so far as the cohesion of a liquid is an index of the average intensity of the stray field in a liquid, it might be expected that the free surface energy between the given liquid A and a fluid phase B would thus increase as the cohesion in B decreases, *provided the thickness of the surface film remains constant.* The values of the cohesion which should be used in such a comparison are not, however, those for pure liquids, but should be the results obtained for the saturated solution of each liquid in the other—if equilibrium values are desired. It is manifestly true that the equilibrium value of the interfacial free energy between miscible liquids is always zero.

With dilute solutions, however, this last condition is not important. Let the two phases be a and b, with the phase a consisting of the constituent A, which we will suppose to be water in all cases. Let the phase b be water vapor B in one case, and benzol B' in another. The drop in intensity between the electromagnetic fields which meet at the interface between water and vapor is much greater than that between water and benzol, since the intensity in a dilute vapor is almost zero. This is illustrated by Fig. 16.

Suppose that a constituent C, a polar-homopolar substance such as butyric acid, is distributed between the two phases. If this passes into the interface in either case it makes the transition from one phase to the other less abrupt by increasing the thickness of the film.

The drop in the intensity of the stray field shown in Fig. 16 may be considered as a restraining and an orienting force, similar to that existing in the field in air between the north and south poles of a

magnet; and the molecules which are oriented as similar to small magnetized needles between them. The restraining force on the needles increases as the rate of fall of the magnetic intensity increases (increase of magnetic flux, or in the number of lines of force), so the restraining force holding the molecules might be expected to increase with the total drop of intensity of the stray field between the two phases, since the molecules of C in the interface bridge the total distance between the two phases.

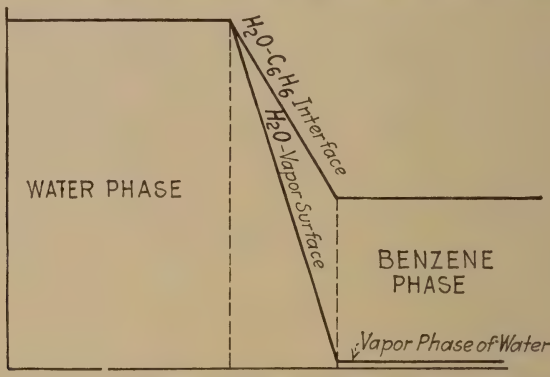

FIG. 16.—The drop in intensity between the electromagnetic fields which meet at the interface between water and vapor, and between water and benzol.

If the molecules of C are thus held in the interface by a restraining force the molar activity or the molar *fugacity* (molar-escaping tendency) of C will be much less in the interface than in either of the two-volume phases, so that the concentration of C in the interface must be much greater than that in either of the volume phases to give a condition of equilibrium.

Since the fall of intensity at the interface water-vapor is much greater than that between water and benzol, the restraining force is much greater in the former case, so the average activity of the molecules of C will be much less at the water-vapor interface; and, therefore, to give equilibrium, the diffusion pressure of C in the two phases *water-vapor* will be much less, to give a certain concentration of C in the interfacial film, than when the two phases are *water-benzol.* This is true so long as the thickness of C does not increase beyond that of a monomolecular layer.

The data obtained in the experiment indicate that in the monomolecular film between water and benzol the butyric acid

molecules have about 3.5 times the activity which they have in the monomolecular film between water and vapor. This demonstrates that the water-vapor interface is by far the more efficient trap, even though the total number of molecules it can hold is conditioned by the area available, and is, therefore, no larger than the number at the interface water-benzol.

A series of experiments by Harkins and Grafton has given the areas per molecule for the mono and dihydroxy derivatives, and one of the trihydroxy derivatives of benzol. The areas are as follows for the most concentrated films:

Compound	Area in A. U.
Phenol	36.6
Pyrocatechol (ortho)	55.3
Resorcinol (meta)	96.0
Hydroquinol (para)	(185.0)
Pyrogallol	42.7

The result for hydroquinol is not comparable with the others, since the film for this substance has not reached the constant composition needed for a monomolecular film. It is evident that the area occupied by the dihydroxy compounds increases rapidly from ortho to meta to para, since the curve for hydroquinol indicates a much higher value than 96 in the constant film, which is not reached on the saturated solution.

The orientation of derivatives of benzol has been considered by Langmuir,[11] and by Harkins, Davies, and Clark,[12] but, on account of the fact that the structure of benzol is unknown, space cannot be given to such a complicated subject in this short review. It may be mentioned, however, that the surface energy of the dinitro benzols is highest for the meta, and lowest for the para, derivative, which seems to indicate that the active portions of the molecule are most easily buried when the two like groups are in the para position. With two different active groups which differ in activity, the para compound usually has the highest, instead of the lowest, total surface energy, which indicates, presumably, that the lack of balance between the groups in the para position causes one of them to be raised into the upper part of the surface.

Surface Energy and Hydrogen Ion Concentration

The importance of the hydrogen ion concentration in connection with the phenomena exhibited by colloidal solutions has recently been emphasized by Loeb, and it is evident that acids and bases also play an important rôle in influencing the surface and interfacial energy relations of certain types of solutions. For example, it was found by Harkins and Ewing[19] that the interfacial tension between $\beta\beta$ dichloroethylsulfide (mustard gas) and water is lowered 55 per cent (from 28.36 to 12.78 dynes per centimeter) at 25°, if the aqueous phase is made 0.1 N with respect to sodium hydroxide, while a lowering of 35 per cent is produced if it is given the same concentration with respect to sodium carbonate. On the other side of the neutral point the interfacial tension is very slightly greater than for pure water, the increase due to tenth normal hydrochloric acid being only 0.54 dynes per centimeter. The use of a dilute alkaline solution of turkey red oil reduced the surface tension by 80 per cent, when the concentration of the oil in the water was 1 per cent, and of the sodium carbonate, 0.1 N.

The interfacial tension between water and ethyl oleate was found by Harkins and Mulliken to be 21.34. With 0.1 N sodium hydroxide this value fell to the remarkably low value 0.3 dyne, possibly the lowest value ever obtained for an interfacial tension with an aqueous phase except when a soap is added. A plot of the interfacial tension against the logarithm of the OH^- concentration has the form of a typical adsorption curve. The results with ethyl oleate are evidently not due to adsorption of OH^- ions, but to the adsorption of sodium oleate formed by hydrolysis of the ester. Similar results, but not so marked, were given by ethyl capronate, and by methyl hexyl ketone, and to some extent by chloroform. With secondary octyl alcohol, neither acid nor alkali produced any appreciable change.

The effect of the addition of acids or bases is very marked with certain solutions. For example, the surface tension of a 0.1 N solution of sodium nonylate is 20.18 dynes per centimeter. The addition of sodium hydroxide to the solution increases the surface tension with extreme rapidity, at 0.001 N to 33.37, and at

0.008 N to 48.82. This effect is evidently due to the repression of the hydrolysis. Further increase in the concentration of the sodium hydroxide gradually *reduces* the surface tension, and in a linear relation to the hydroxyl ion concentration.

The above results seem to indicate that the marked effects of acids and bases upon the interfacial or surface tensions of certain substances are due to chemical changes in the substances much more than they are to the adsorption of hydrogen or hydroxyl ions.

Table IV shows the remarkable effects of certain salts upon a film of sodium oleate. The data were obtained by Harkins and Thomas, and were secured by a repetition of the work of Clowes[31] in such a way as to obtain surface energy values instead of the number of drops given by a certain pipette.

TABLE IV.—EFFECTS OF THE ADDITION OF SALTS UPON THE INTERFACIAL TENSION WITH A FILM OF SODIUM OLEATE (OLEIC ACID WAS ADDED TO EACH OIL TO A CONCENTRATION OF 0.001 M)

Base or salt added to aqueous phase			Surface tension in dynes per square centimeter	
NaOH	NaCl	$CaCl_2$	Olive oil	Paraffin oil
Mols per liter				
.....	....	.....	24.11	31.05
0.001	....	.....	7.3	7.2
0.001	0.15	.....	0.002	0.00
0.001	....	0.0015	9.88	9.65
0.001	0.15	0.0015	6.88	7.48
0.001	0.30	0.0030	6.36	7.12
0.001	0.45	0.0045	6.70	7.36
0.001	0.60	0.0060	7.31	8.20

Thus while calcium chloride, the salt of a bivalent metal, increases the interfacial tension, sodium chloride reduces it very greatly. Thus when the aqueous phase was 0.001 molar with respect to sodium hydroxide, and 0.15 molar with respect to

sodium chloride, the interfacial tension toward the oils 0.001 molar with respect to oleic acid was 0.002 for olive oil, and 0.00, or too low to be measured, for the paraffin oil (purified stanolax).

Surface Energy in Colloid Systems

As has been emphasized by numerous writers, the importance of the surface energy of any system increases rapidly as its particles become smaller. Thus, if a sphere of water 1 cm. in diameter is converted into a fog of minute drops 0.1μ in diameter, the surface is increased 100,000 times, or to an area about 1 by 30 m. Accompanying this change the total surface energy increases from about 0.00009 cal., an amount altogether imperceptible in ordinary measurements of heat, to about 9 cal., which is nearly one-fourth the latent heat of fusion for this amount of liquid. For particles 0.01μ in diameter the surface energy becomes more than twice the latent heat of fusion.

There is no sharp distinction between systems which are and are not colloidal, but a colloidal system may be defined as one in which the surface energy is appreciable in comparison with the heat of fusion or of vaporization of the material present as the dispersed phase.

According to the equation developed by W. Thomson,

$$\frac{RT}{M} \ln \frac{p_2}{p_1} = \frac{2\gamma}{\rho}\left(\frac{1}{r_2} - \frac{1}{r_1}\right)$$

the vapor pressure of a particle depends upon its surface tension and increases as the size of the particle decreases. Thus, a drop of water of radius 1μ has a vapor pressure only 0.1 per cent greater than a plane surface; for a radius 0.01μ it is 10 per cent, and at $1\mu\mu$, 100 per cent greater.

The similar equation of Ostwald and Freundlich replaces the pressure p in this equation by the solubility s, and is

$$\frac{RT}{M} \ln \frac{s_2}{s_1} = \frac{2\gamma}{\rho}\left(\frac{1}{r_2} - \frac{1}{r_1}\right)$$

Here M is the molecular weight of the substance, ρ its density, and r is the radius of the particle. Thus, it is evident that the relations in any colloidal system are highly dependent upon the magnitude of the surface tension.

It is evident that the surface tension of a surface depends upon its curvature. Langmuir[11] considers that the shape of the molecules in the surface film determines the size of colloidal particles. Thus, in discussing the orientation theory he states:

> This theory also affords an explanation of the mechanism by which colloids are formed. If a film of closely packed oleic acid molecules covers the surface of water to which sodium hydroxide has been added, OH groups are absorbed by the COOH radicals, causing an expansion of the lower side of the film without a corresponding expansion of the upper side. This results in the bulging of the film downwards in spots, so that it finally detaches itself in the form of particles, the outer surface of which consists of COOH groups together with the absorbed OH, while the interior consists of the long hydrocarbon chains.
>
> The size of the colloidal particles is determined by the difference in size between the two ends of the molecules, just as the size of an arch is dependent upon the relative sizes of the two ends of the stones of which the arch is constructed.

Emulsions

Harkins, Davies, and Clark[12] determined the surface energy variation with the concentration for sodium oleate, a substance of importance in the formation of emulsions, and came to the conclusion that the formation of emulsions by emulsifying agents of the type of soaps is due to the formation around the drops of a film of adsorbed molecules (together with some molecules of the acid formed by hydrolysis, and some of the acid ions, oleate, stearate, and similar ions). The number of these ions is probably not very great, since otherwise the oil drop would be more highly charged with negative electricity than is actually the case. Work upon the effects of acids and bases upon surface tension seemed to indicate that the great effect of hydrogen ion concentration is not produced directly through the adsorption of hydrogen or hydroxyl ions, but through their effect upon the hydrolysis of the soap, which changes the surface tension markedly, as was shown in the section on the effects of acids and bases upon surface tension. The following quotation is of interest in giving some of the details of this theory.

> In order to illustrate this effect, we have chosen for investigation a substance, sodium oleate, in which the paraffin chain is so long that it

is very highly adsorbed. While many investigations of this kind have been made, in none of them, so far as we have been able to discover, have accurate methods been employed, and this substance was chosen because it is adsorbed so greatly that it is extremely efficient in the formation of emulsions. The hydrocarbon chain is so long that even though it is an unsaturated substance, oleic acid is insoluble in water, so that, since sodium oleate is partly, though not highly, hydrolyzed by water, there is the additional complication in this case that the acid may separate out as a colloid. It would be expected that the sodium oleate or the oleic acid, in so far as they are adsorbed in the molecular form, would be set with the $-COOH$ or $-COONa$ group toward the water. Now, the paraffin chain is so insoluble that, even when a colloid is not visible, it is found by investigations on the conductivity of such solutions (McBain) that the ions have formed very heavy multiply charged aggregates or micelles. These aggregates carry a negative charge, and would seem to consist of a considerable number of the negative ions of the salt. The formation of these aggregates is quite likely connected with the insolubility of the hydrocarbon chains, and they form with the saturated compounds, such as sodium palmitate, just as they do with the oleate.

This idea was also applied to the inversion of emulsions, and to their stability, as conditioned by the shape and orientation of the molecules.

When Newman, working with Bancroft in 1914, found that, while sodium oleate in solution will give emulsions of benzene in water, and the oleate salts of a metal with a valence higher than one will give emulsions of water in benzol, we were working experimentally in this laboratory on the adsorption of these long hydrocarbon chains. Now, while Bancroft seemed to think that this work indicated that the liquid with the higher surface tension forms the inner phase, it seemed to us that the only apparent relation was that to the *number of oleate radicals* in the molecule of the protective colloid (sodium oleate, or magnesium oleate). Therefore, it quite possibly may be the orientation—(according to the theory presented in this paper, molecular orientation in the interface *is* the factor which does determine the stability of emulsoid particles and also the sign and magnitude of the electromagnetic field at the surface of the drop; it should be noticed that all of the best commercial emulsifying agents have *very long molecules*)—and the form of the molecules, together with adsorbed ions in the interface between the dispersoid particles (or small drops), and the dispersion medium which determine the surface energy relations, and, therefore, the size of the drop at which it becomes stable. In other words, this idea is that the drop would be

stable whenever the molecules, together with adsorbed ions, etc., in the interface fit the curvature of the drop. The molecules in the curved surface would not need to be all of the same kind. If the molecules do

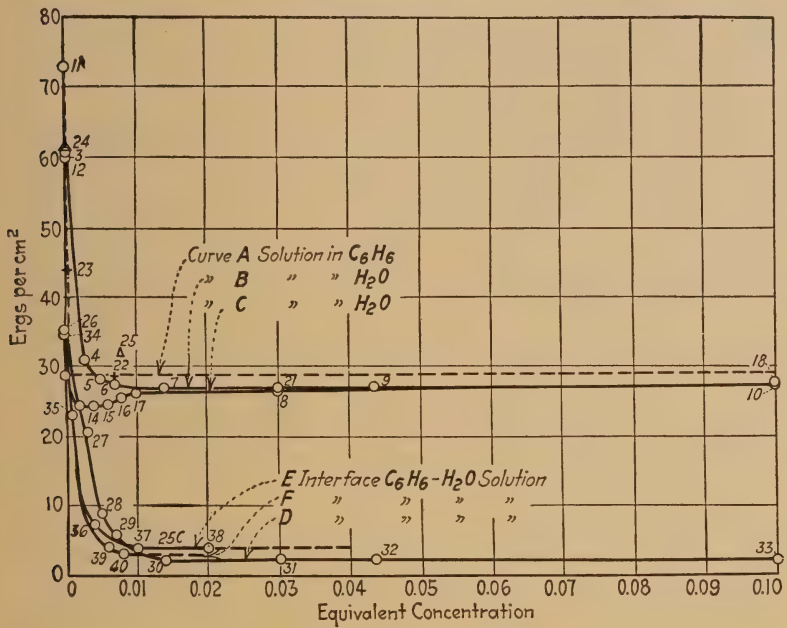

FIG. 17.—The effect of sodium oleate upon the free surface energy of water, and also at the interface between water and benzol. The heavy horizontal lines indicate *saturated films*. (A saturated film is by definition one whose surface tension does not change with the concentration of the solution. All films that are not monomolecular are saturated.) Curve *A* indicates that a saturated solution of sodium oleate in benzol has practically the same surface tension as pure benzol. Curve *D* represents the interfacial tension between two layers obtained by rotating aqueous sodium oleate solutions with benzol and allowing to stand until the next day. Curve *B* shows the values for the surface tensions of the aqueous sodium oleate phase after rotating with the benzol as for Curve *D*. Curve *E* indicates the interfacial tension between benzol and aqueous solutions of sodium oleate when no emulsification or rotation had taken place. Curve *F* represents the data for the interfacial tension between the layers after the aqueous solutions of sodium oleate were shaken vigorously with about one part of the benzol to 20 parts of the solution. This is the best of the methods studied for determining the interfacial tensions, since the benzol dissolves practically no sodium oleate. Curve *C* gives the data for the aqueous solutions of sodium oleate in air. It shows that the surface tension drops off very rapidly until at a concentration of about 0.002 N we have the lowest surface tension.

not fit in the curved surface, the drop will not be perfectly stable, and will either decrease or increase in size if given time.

From the standpoint of this idea of molecular orientation and molecular fitting, the free surface energy of small drops should vary with the radius of curvature (in addition to the pressure effect which is usually taken into consideration), and we have been working on the surface energy relations of large drops (curvature so large as to be practically planes from the standpoint of the results) only as an introduction to work on the surface-tension relations at highly curved surfaces.

Figure 17 presents some very interesting relations. Thus 0.0001 M sodium oleate reduces the surface tension of water from 72.8 to 60.46 ergs per cm^2., and even when 0.0002 M sodium hydroxide is added, to prevent hydrolysis, the surface tension goes as low as 61.32, so the oleate film builds up with extreme rapidity. A 0.014 M solution decreases the interfacial tension from 35 to 2.22, or to about 6 per cent of its former value. Both the curve at the air-liquid and at the benzol aqueous solution interface, indicates that the adsorption is enormously rapid at first, and that for the vapor-solution interface at as low a concentration as 0.002 M the adsorbed film has become so closely packed that further increase in the concentration of the solution no longer lowers the surface tension. Thus these films become saturated at extremely low concentrations of the saturating substance. These experiments show that sodium oleate will cause the benzene to form the emulsoid drops even when the outer phase has the higher surface tension when measured alone with a plane surface. It is also of interest that even for a plane surface the interfacial tension drops very low for the solutions which form stable emulsions, and that the value falls as low as 2 ergs. per cm^2. or even less in one case, so the curvature of the surface would not have to produce a very large effect to reduce the surface tension to zero.

Figure 6 represents this theory in the form of highly conventionalized drawings. The molecules act as oriented truncated cones, but in two dimensions as wedges, so this may be called the oriented wedge, or truncated cone, theory of emulsions. The conical shape of the molecule is conditioned by the relative areas of the cross-sections of the head, or polar part of the molecule, and of the hydrocarbon chains at the other end. The most pronounced changes occur when two or three $CH_3(CH_2)_nCOO-$

groups are substituted for one, since this always changes the emulsion from drops of oil in water, to drops of water in oil. The size of the drop is not that which would be calculated from the shape of the molecular truncated cone, since the shape of the drop is affected by a staggering of the molecules in the film (subfigure 3), by the presence of some molecules of the acid, and by a few of the acid ions. It is found, for example, that drops of oil in water are much larger than would be expected from the shape of the molecular truncated cones. A further prominent factor in bringing this about is that molecules of oil from the drop undoubtedly penetrate between the hydrocarbon chains of the soap and thus reduce the effect of the conical shape. This factor has not been taken account of in the drawing, which has been made as simple as possible.

Finkel, Draper and Hildebrand have shown that the size of the drops, and the stability of the emulsions, vary with the dimensions of the polar head of the soap molecules in just the order specified by the theory proposed by Harkins.

Figure 18 gives results which have an important bearing upon the application of the orientation theory to the subject of emulsions. They give evidence in favor of the particular theory of emulsions advanced in 1917 by Harkins, Davies, and Clark. According to this theory the sizes of drops in an emulsion produced by the use of a soap as an emulsifying agent depend upon the shapes of the molecules in the film around the drops. In an emulsion produced by sodium oleate, it may be assumed that the film contains sodium oleate, oleic acid, and oleate ions. In the experiments of Harkins and Keith, represented in the figure, the peak in the curve for sodium oleate comes at 4 microns (4×10^{-4} cm.). If a sodium oleate molecule has a length of 28×10^{-8} cm., as accords with work on the thickness of films, the length of the molecule is only $\frac{1}{750}$ of the radius of the drop, and to fit into such a surface the polar end of the molecule would need to have a cross-section with a diameter only $\frac{1}{750}$ greater than that of the non-polar end. Now what data we have indicate a much greater difference than this, so it would seem that in this case the size of the drop is not entirely determined by the shape of the molecule of soap.

The addition of sodium hydroxide to the partly hydrolyzed sodium oleate would repress the hydrolysis, and should, according to the theory, produce a considerable diminution in the size of the drops of oil in the emulsion. The figure indicates that when the 0.1 M sodium oleate solution was made 0.1 M in sodium hydrolysis, a remarkable change in the size of the drops was obtained, since the diameter was decreased to only one-

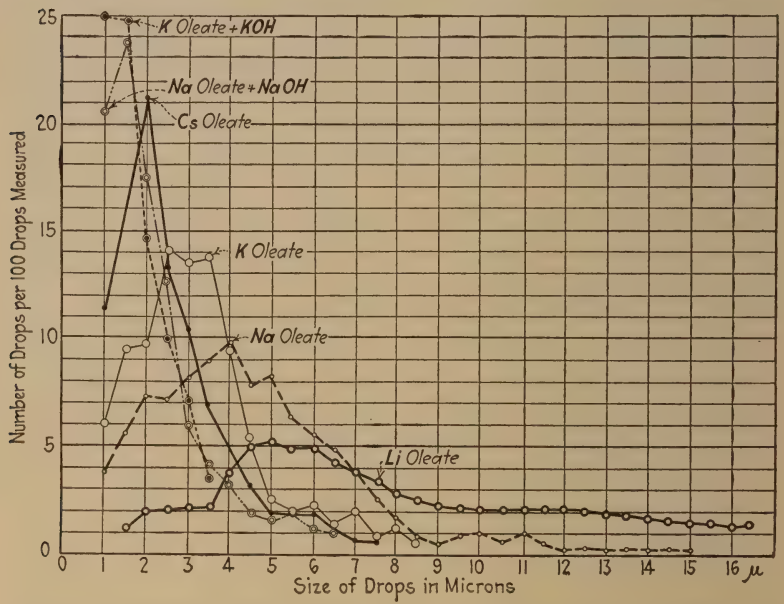

FIG. 18.—Relation between the size of the polar end of a molecule (as increased by passing from a Na soap to the K and Cs soaps), and the size of the emulsified oil drops; and the effect of hydrolysis on the size of the drops.

third of that obtained when the soap was used alone. The figure indicates that as the size of the polar end of the molecule is increased by a change from the lithium soap to the sodium, the potassium, and the caesium soap, the size of the emulsified oil drops decreases, and the peak in the curve becomes higher and higher. Finkle, Draper, and Hildebrand found a similar shift in size, but not such an increase in the height of the peak, in the change from a sodium to a potassium, and to a caseium soap. The figure shows that with potassium oleate, when its

hydrolysis is repressed by potassium hydroxide, the peak lies higher and at smaller sizes of the oil drops than is found for similar emulsions with sodium hydroxide. The relative shift of the peak between sodium oleate with sodium hydroxide, and potassium oleate with potassium hydroxide, amounts to about one-fourth of the diameter of the drop, which is about the same as is found when the soaps are used alone.

The sizes of the drops are changed by a change in the oil which is emulsified, and is in the direction of larger drops as the viscosity increases. The addition of oleic acid is found to have a marked influence upon the sizes of the drops.

Thus it is found that a repression of hydrolysis, or a change in the size of the atom of the metal, produces a shift in the size of the emulsified drops in the direction specified by the particular form of the wedge (or truncated cone) theory of emulsions and the inversion of emulsions (see Fig. 6) suggested by Harkins, Davies, and Clark in 1917. However it is true that the sizes of the drops is always larger than would result if the film were made "unstaggered" and consisted of molecules of soap alone, which fact was recognized when the theory was suggested.

The form of the curve of distribution for the sizes of the drops, as given in the figure, seems to be much like that of the distribution of molecular speeds according to the theory of Maxwell. All of the curves, except perhaps that for lithium oleate, seem to be of the same general form. The points plotted in the figure represent the actual measurements, and there has been no rounding off in order to improve the smoothness of the curves. The lower right-hand portion of a number of the curves has been omitted in order to avoid confusion due to the great number of points in this part of the figure. The area under any one curve is the same as that under any other.

As has been stated, a change in the oil which is dispersed in an emulsion produces a remarkable change in the size of the drops, even when the emulsion is prepared in exactly the same way. Thus the most probable size for sodium oleate emulsions prepared by Harkins and Keith, was found to be 9.2μ for stanolax, 3.9μ for octane, and 1.94μ, for benzol or mesitylene. Table V gives the most probable size, that is the peak in the curve, for various emulsions as obtained by the use of a carefully standardized method of preparation.

TABLE V.—SIZES OF DROPS IN EMULSIONS OF VARIOUS OILS IN 0.1 M SOLUTIONS OF OLEATE SOAPS (HARKINS AND KEITH)

1 Soap	2 Added reagents	3 Size at peak	4 Per cent of drops at peak	5 (3) × (4)
		Octane		
Lithium	.....	4.75	7.25	34.4
Sodium	.....	3.90	9.5	36.0
Potassium	.....	2.90	13.3	38.5
Rubidium	.....	2.50	17.00	42.5
Caesium	.....	1.95	21.2	41.3
Sodium	0.1 M sodium hydroxide	1.45	23.8	34.5
Potassium	0.1 M potassium hydroxide	1.2	(28)	33.0
Sodium	0.1 M oleic acid in oil	1.45	27.3	39.6
		Stanolax		
Sodium	.....	9.2	3.7	34.0
Potassium	.....	6.9	4.91	33.9
Caesium	.....	4.6	6.08	28.0
Sodium	0.1 M sodium hydroxide	5.75	4.13	24.0
Sodium	0.1 M oleic acid in oil	4.6	7.83	36.0
Sodium	0.1 M sodium chloride	5.75	5.22	30.0
Sodium	0.1 M potassium iodide	6.9	4.08	28.2
		Benzol		
Sodium	.....	1.94	19.82	38.4
		Mesitylene		
Sodium	.....	1.94	21.1	41.0

The oil drops in an emulsion carry a negative charge. The effect of a charge is to keep the drops apart by repulsion, and to decrease the surface tension by giving the drop a tendency to expand. Both of these effects increase the stability of an emulsion or any other colloid. The potential difference at the interface between two liquids, or between a liquid and a solid, may be changed by a variation in the hydrogen ion concentration. It has been shown by Powis that the stability of dilute oil in water emulsions (without the presence of a soap) persists at a P.D. greater than 0.03 volt, but that within the range ± 0.03 the stability disappears. Different types of bacteria, for example, exhibit different ranges for this zone of instability. The instability is, in general, greatest at the isoelectric point (Hardy).

Preliminary determinations of the cataphoresis of the oil drops in emulsions in oleate soaps have been made for the writer by Professor Falk of the University of Chicago. They show that the oil drops carry a negative charge, and that the P.D. is about 0.06 volt for emulsions produced by sodium, potassium and caesium oleates. The numerical value is considerably decreased by the addition of either sodium hydroxide or sodium chloride to the aqueous phase in which sodium oleate is the emulsiying agent.

The changes produced in the surface energy of an interface by electrical charges, and by the nature and magnitude of the P.D., are of fundamental importance in connection with the stability of colloids, and will be discussed in connection with the treatment of colloid systems in various other chapters.

The Thermodynamics of Surfaces

The most fundamental relations in connection with surface energy are easily developed by the application of the principles of thermodynamics.

The interfaces commonly called "surfaces" are of several kinds: liquid-vapor, liquid-liquid, liquid-solid, and solid-solid. The thermodynamics of saturated films has been treated by Dupré,[3] Lord Rayleigh,[27] and, more thoroughly, by Gibbs[4] and by Einstein.[28] The following treatment is somewhat different from that presented by any of these workers, and has some advantages.

The surface film may be either saturated or unsaturated, and a part of the treatment presented will be applicable to either case.

Let S = the entropy of the whole surface, s of unit area
U = intrinsic energy of the total surface
u = the intrinsic energy of unit area
γ = the free surface energy per unit area, or the surface tension per unit length
c = the specific heat of the surface, where specific refers to unit area and not to unit mass
A = the area of the film
l = the latent heat of the surface per unit area
Q = the total heat added to the surface

These quantities may be thought of as applying to a film of infinitesimal thickness, but, since this is not the true thickness for the actual film, they represent the surface densities. Thus U, as Gibbs states, denotes the excess of the energy of the actual mass which occupies the total volume considered, over that energy which it would have if on each side of the surface the density of energy had the same uniform value quite up to that surface which it has at a sensible distance from it.

From the first law

$$dQ = d(Au) - \gamma dA = A\frac{\partial u}{\partial T}dT + \left[A\frac{\partial u}{\partial A} + (u - \gamma)\right]dA \qquad (1)$$
$$= C dT + l dA$$

This equation is perfectly general.

We will define c as follows:

$$c = \frac{1}{A}\left(\frac{dQ}{dT}\right)_{dA=0} = \frac{du}{dT} \qquad (2)$$

Equation (1) now becomes:

$$dQ = Ac\,dT + l\,dA = AC\,dT + (l + \gamma)\,dA - \gamma dA. \qquad (3)$$

Let the film be saturated, and the definition of a saturated film will be that u and γ are functions of T only.

$d(Au) = A\frac{du}{dT}dT + u\,dA = Ac\,dT + (1 + \gamma)dA$ is an exact differential. (4)

and

$$c,\ l = f(\mathrm{T}) \text{ only.} \tag{5}$$

$$c = \frac{\partial}{\partial \mathrm{T}}(l + \gamma) = \frac{du}{d\mathrm{T}} \tag{6}$$

$$u = l + \gamma \tag{7}$$

$$l + \gamma = \int c\ d\mathrm{T}, \text{ and is a definite function of T.} \tag{8}$$

From the second law

$$d\mathrm{S} = \frac{d\mathrm{Q}}{\mathrm{T}} = \frac{\mathrm{A}c}{\mathrm{T}}\,d\mathrm{T} + \frac{l}{\mathrm{T}}\,d\mathrm{A} \text{ is an exact differential.} \tag{9}$$

$$\frac{c}{\mathrm{T}} = \frac{\partial}{\partial \mathrm{T}}\left(\frac{l}{\mathrm{T}}\right) \text{ or } c = \frac{\partial\left(\frac{l}{\mathrm{T}}\right)}{\partial \ln \mathrm{T}} \tag{10}$$

Combine (6) and (10), and

$$\mathrm{T}\frac{\partial}{\partial \mathrm{T}}\left(\frac{l}{\mathrm{T}}\right) = \frac{\partial}{\partial \mathrm{T}}(l + \gamma) \tag{11}$$

$$\frac{\partial l}{\partial \mathrm{T}} - \frac{l}{\mathrm{T}} = \frac{\partial l}{\partial \mathrm{T}} + \frac{\partial \gamma}{\partial \mathrm{T}}$$

or

$$l = -\mathrm{T}\frac{\partial \gamma}{\partial \mathrm{T}} = -\frac{\partial \gamma}{\partial \ln \mathrm{T}} \tag{12}$$

Equation (7) now becomes

$$u = (\gamma + l) = \gamma - \mathrm{T}\frac{\partial \gamma}{\partial \mathrm{T}} \tag{13}$$

$$c = \frac{\partial}{\partial \mathrm{T}}\left(\gamma - \mathrm{T}\frac{\partial \gamma}{\partial \mathrm{T}}\right) = \frac{\partial \gamma}{\partial \mathrm{T}} + \frac{\partial l}{\partial \mathrm{T}} = \frac{\partial l}{\partial \mathrm{T}} - \frac{\partial l}{\partial \mathrm{T}} - \mathrm{T}\left(\frac{\partial^2 \gamma}{\partial \mathrm{T}^2}\right)$$

or

$$c = -\mathrm{T}\left(\frac{\partial^2 \gamma}{\partial \mathrm{T}^2}\right) \tag{14}$$

Equation (1) is fundamental for saturated and unsaturated surfaces, and equations (13) and (14) for saturated films.

The experimental results indicate that over moderate ranges of temperature γ is a linear function of the temperature, or $\frac{d\gamma}{d\mathrm{T}} =$

k. So long as this is true, u, the total surface energy per unit area, is independent of the temperature. This constancy of u makes it a much more characteristic function than either the free surface energy or the latent heat of the surface (1). Table III shows that, indeed, the total surface energy is not only largely independent of temperature, but is also very characteristic of any special class of compounds. In so far as γ deviates from a linear function, u will vary with the temperature, so that even a greater regularity might have been obtained by calculating u from data taken at corresponding states. However, the regularities in the values of u as they have been obtained are extremely striking.

So long as $\frac{d\gamma}{dT}$ is a straight line, c, which is equal to $-T\frac{d^2\gamma}{dT^2}$, is zero; or the superficial specific heat is zero, as was found by Einstein. This indicates that *under this condition* all of the energy of formation of a surface ($= u$ or $\gamma + l$) goes into the surface in a potential form, and this, in turn, seems to show that the energy is stored up by some configuration of the surface layer. The fact that the total surface energy is almost independent of the temperature indicates that this configuration is almost the same for various temperatures, but it is quite likely that there may be some change in the relative distances of the molecules due to thermal expansion.

If we now imagine that inside a liquid, a plane area of 1 sq. cm. exists, and then pull the liquid apart over this area, so that two surfaces each 1 sq. cm. in area are formed, then, as shown previously the increase in free energy is 2γ. Now equation (13) shows that at the same time there is a cooling of the surface equal to $2l$, so that the kinetic energy of the molecules aids in pulling the surfaces apart. The total energy $2u$ involved in this process may be imagined to be used up (1) in giving orientation to the two sets of molecules on both sides of the imaginary plane, while still in the liquid, and (2) in pulling the two oriented surfaces apart. By this it is not meant that the process takes place in this order, but only that the end result is the same as the result of these two steps. While we have at present no way of determining the relative amounts of energy involved in the two steps, it would seem that the amount of energy involved in (1) is rela-

tively small, and that the greater amount is that of step (2). Now, if we knew the laws according to which the electromagnetic forces vary in the fields between and in the molecules which make up the surface layers, it would be possible to get a solution of our problem. However, since this is not known, it seems better to solve the converse problem, that of determining the rate at which these forces fall off, from the data on surface energy.

Equation (12) indicates that if the free surface energy decreases with the temperature, as is usually the case, the formation of the surface will have a cooling effect, while if it increases with the temperature, as it does in the case of the two anisotropous liquids, ethyl *p*-azoxybenzoate, and ethyl *p*-ethoxybenzalamino-α-methyl-cinnamate, there will be a heating effect. In either case the first effect is to increase the free surface energy. It is evident that a contraction of an ordinary surface lowers its tension, and that the free surface energy of a fresh surface, between two phases which may exist together, is greater than that of an old one. If a surface is thought of as being formed with infinite speed, then the changes which follow are such as to lower the free energy.

From thermodynamics we learn that the arrangement of the molecules in the surface of a liquid must be such as to make the free surface energy γ a minimum. Now, since

$$\gamma = u - \mathrm{T}s \tag{15}$$

and when the change is not isothermal, T changes, and when the change is not reversible, the superficial entropy s changes, the condition for an isothermal reversible change in the surface is that there shall be a decrease in the total superficial energy u just equal to that of the superficial free energy γ, so under the given conditions the configuration must be such as to make the total surface energy a minimum.

If these equations are compared with Fig. 2, which is primarily due to Jaeger,[29] it is seen that the relations indicate that the specific heat of the surface is not wholly independent of the temperature, and that it approaches zero with extreme rapidity as the critical temperature is approached, so the surface film thickens rapidly and rapidly loses the orientation of its molecules just before the critical temperature is reached.

The Determination of Surface Tension

The surface tension of a liquid may be determined by any one of a considerable number of methods, the most widely used of which are known as the drop weight and the capillary height methods. These methods have been studied critically: the former by Harkins and Brown, and the latter by Richards and Coombs.[32]

REFERENCES

Books

1. Freundlich, H.: "Kapillarchemie," Leipzig, 1923.
2. Willows and Hatschek: "Surface Tension and Surface Energy," Philadelphia, 1923.
3. Dupré: "Theorie Mecanique de la Chaleur," Paris, 1869.
4. Gibbs: Scientific Papers, vol. 1, 1906.

Papers

5. Pockels, Miss A.: *Nature*, **43** (1891), 437.
6. Rayleigh, Lord: *Phil. Mag.*, **48** (1899), 331.
7. Devaux: Papers 1903 to 1913 reviewed in Ann. Report Smithsonian Inst., 1913, pp. 261–73; *Soc. Franc. phys.*, **55** (1914), 3; **57** (1914), 3.
8. Marcelin: *Ann. Phys.*, **1** (1914), 19.
9. Labrouste: *Compt. rend.*, **158** (1914), 627.
10. Hardy: *Proc. Roy. Soc.*, **A, 86** (1911–12), 634; **88** (1913), 303–33.
11. Langmuir: *Chem. Met. Eng.*, **15** (1916), 468.
12. Harkins, Brown and Davies: *J. Am. Chem. Soc.*, **39** (1917), 354; Harkins, Davies and Clark: *Ibid.*, **39** (1917), 541.
13. Harkins and Cheng: *Ibid.*, **43** (1921), 36; Harkins, Clark and Roberts: *Ibid.*, **42** (1920), 700.
14. Harkins and Roberts: *Ibid.*, **44** (1922), 653.
15. Langmuir: *Ibid.*, **39** (1917), 1848.
16. Adam, N. K.: *Proc. Roy. Soc.*, **A, 101,** 452.
17. Harkins and Ewing: *J. Am. Chem. Soc.*, **42** (1920), 2539; Harkins and Feldman: *Ibid.*, **43** (1921), 2665.
18. Traube, J.: *Lieb. Ann.*, **265** (1891), 27.
19. Harkins: *Proc. Nat. Acad. Sciences*, **5** (1919), 544.
20. Lunn: *J. Am. Chem. Soc.*, **41** (1919), 986.
21. Donnan and Barker: *Proc. Roy. Soc.*, **A, 85** (1911), 557.
22. Drucker: *Z. physik. Chem.*, **52** (1905), 641.
23. Whatmough: *Ibid.*, **39** (1902), 129.
24. Szyszkowski: *Ibid.*, **64** (1908), 385.
25. Milner: *Phil. Mag.* (6), **13** (1907), 96.

26. HARKINS and EWING: *J. Am. Chem. Soc.*, **41** (1919), 1977.
27. RAYLEIGH, LORD: *Phil. Mag.* (5), **30** (1890), 461.
28. EINSTEIN: *Ann. Physik.*, **4** (1901), 513.
29. JAEGER, F. M.: *Koninkl. Akad. Wetensch.* Amsterdam, **17** (1914), 329, 365, 386, 395, 405, 416, 555, 571; *Z. anorg. Chem.*, **101** (1917), 1.
30. RAYLEIGH: *Sci. Papers*, III, 562.
31. CLOWES: *J. Phys. Chem.*, **20** (1916), 408.
32. Determination of Surface Tension, Review and Bibliography, FERGUSON, Fifth Report on Colloid Chemistry, London, 1923, p. 1. Capillary Height Method, RICHARDS and COOMBS, *J. Am. Chem. Soc.*, **37** (1915), 1643. Drop Weight Method for Interfaces, HARKINS and HUMPHREY, *ibid.*, **38** (1916), 242. Drop Weight Method for Surfaces, and Correction Curve, HARKINS and BROWN, *ibid.*, **41** (1919), 499.
33. HARKINS and KING: *J. Am. Chem. Soc.*, **41** (1919), 970.

CHAPTER VII

THE THEORY OF EMULSIFICATION

By

Joel H. Hildebrand

When two incompletely miscible liquids are mechanically agitated so as to disperse one of them in the other in the form of droplets, an amount of work must be performed upon the system which is equal to the product of the interfacial tension by the increase in surface. This work may be considerable, and accounts for the fact that emulsions made from two pure liquids are always unstable, the coalescence of the droplets upon contact liberating the stored energy. To stabilize an emulsion, therefore, it is necessary to add some third substance which is capable of producing a film which will prevent the coalescence of the drops. The conditions for the stability of such a film are, in part, the same as those which give stability to the liquid film between the bubbles of a foam, or "emulsified gas."

Adsorbed Films

In the first place, the work done by coalescence of the drops is diminished by diminishing the interfacial tension. An emulsifying agent, therefore, which considerably reduces the interfacial tension also reduces the tendency towards coalescence. Such an agent also has a further stabilizing effect upon the film separating two droplets similar to the effect of soap and other foaming agents upon the stability of the liquid film separating two bubbles in a foam.[1] This effect is brought about as follows: Whenever a substance lowers a surface or interfacial tension it tends to diffuse into the surface and to become there more concentrated than in the interior of the liquid.[2] At a fresh surface, before diffusion has had time to establish the adsorbed layer, the surface tension is higher than at an old surface. Rayleigh has given figures for

the surface tension of soap and saponin solutions obtained by both dynamic and static methods, here reproduced in Table I, which show the great difference that may be obtained.

TABLE I

Liquid	Surface tension	
	Static	Dynamic
Water	75	75
0.025 per cent sodium oleate	55	79
0.25 per cent sodium oleate	26	79
2.5 per cent sodium oleate	26	58
Saponin solution	52	73

Accordingly, if a film of soap solution separating two bubbles (or drops of oil) be threatened with rupture, the fresh surface produced at the threatened point has a higher surface tension than the adjacent surface, and thus protects itself automatically from further injury. We may, therefore, conclude that a substance which is highly adsorbed at an interface, lowering greatly the interfacial tension, is able to act as an emulsifying agent.

As is well known, the soaps are exceedingly effective emulsifying agents for systems composed of water with some non-polar or oily liquid. Donnan[3] has shown that the lowering of interfacial tension, with attendant effect upon the emulsifying power, increases with the length of the hydrocarbon chain, becoming very marked with sodium caprylate (containing 8 carbon atoms) and increasing rapidly to the higher members.

More recent work by Langmuir[4] and by Harkins[5] and co-workers indicates that the molecules of a soap would tend to orient in the interface so that the paraffin chain is in the non-polar liquid, or oil, while the metallic end is in the water. The insolubility of one end of the molecule in the one liquid and of the other end in the other liquid is peculiarly favorable to adsorption at the interface and consequent low interfacial tension. The size of the molecules, moreover, diminishes the effect of thermal agitation which prevents adsorption of small molecules.

Viscosity

It is evident that the effect of the emulsifying agent upon the viscosity of the external phase of the emulsion should exercise an important influence upon the stability of the emulsion, since the more viscous solution would drain more slowly from the film between two droplets, thus retarding their coalescence. High viscosity also diminishes the Brownian movement, which may otherwise be considerable in highly dispersed emulsions, and which promotes collisions and hence increased opportunities for coalescence. The importance of viscosity for the stability of foams was stated by Plateau,[6] and for emulsions, analogously, by Hillyer,[7] who nevertheless showed the far greater importance of low surface tension, since many cases are known where high viscosity does not yield emulsions, while, on the other hand, low surface tension and excellent emulsions are produced by amounts of soap so small as to have but little effect upon the viscosity. Holmes and Child,[8] on the other hand, have concluded that for gelatin solutions a favorable viscosity is more important than low interfacial tension in yielding stable emulsions.*

The Type of Emulsion and the Nature of the Emulsifying Agent

Although the more familiar emulsions have water as the external, or continuous, phase, and some non-polar liquid or "oil" as the internal or discontinuous phase, it is possible, as was pointed out by Wo. Ostwald,[9] to have emulsions of the inverse type, in which the water is the dispersed phase. Ostwald thought that the type should be determined by the volume-ratio of the two liquids, and that only so much liquid could be dispersed as could be packed as spheres of approximately equal size in the other liquid (about 74 per cent of the total volume) and that the addition of more

*It would seem to the writer desirable to determine whether emulsions prepared in solutions of different viscosity might not be very differently dispersed during their preparation, which would affect the rate of breakdown. It seems difficult otherwise to account for the observation of Holmes and Child that the most favorable viscosity was not the maximum, for it is evident that in an external phase of infinite viscosity there could be no coalescence whatever.

would cause it to become the external phase. We know, however, from the previous work of Pickering,[10] that as much as 99 per cent by volume of oil can be dispersed in a soap solution. The dispersed oil droplets in such an emulsion distort each other so as to form polyhedra,[11] which makes the emulsion elastic, since deformation increases the superficial area of these polyhedra and allows the interfacial tension to act as a restoring force. Such emulsions, like stiff mayonnaise dressing, are, therefore, jelly-like in properties.

In spite of the fact that the dispersed phase may far exceed the other in volume, it is nevertheless easier to make the desired type of emulsion by using an excess of the dispersing phase at the outset, and doubtless, also, using a vessel wet better by this phase than by the inside phase. As the emulsification proceeds, the liquid to be dispersed may be added in larger quantities, since it suffices to have its volume less than that of the emulsion already prepared, rather than that of the external phase first used.

It seems possible to account for the types of emulsion yielded by different emulsifiers most easily in cases where the latter are solid powders. If the solid particles are wetted preferentially by one liquid they go entirely into that liquid. If, however, there is sufficient tendency for both liquids to wet the particles, so that the angle of contact is finite, then the powder collects at the interface. This angle will rarely be 90 deg., so that the particles will usually be more in one liquid than in the other, and this will cause the interface to curve, due to the crowding of the particles in the better wetting liquid, which thus becomes the outer phase.

The data at hand[12] seem to accord with this picture,[13] although, as stated by Clayton,[14] more observations of contact angles are greatly to be desired.

Where the emulsifier is a colloid, the picture may be essentially the same, which leads to the very useful rule of Bancroft,[4] that an oil-soluble colloid may emulsify water in oil, and *vice versa*. The colloid particles must have both polar and non-polar groups upon their surfaces, so as to be adsorbed at the interface, but they will tend to remain more largely in the liquid which is the better dispersing medium for them.

The interfacial film may doubtless vary greatly in thickness, becoming sometimes a veritable skin, but there is good evidence

that they may be so thin as to consist only of a single molecular layer,[15] and that the molecules in this layer are oriented with their polar portions in water, and their non-polar portions in the oil, or other non-polar liquid, as previously stated.

The rôle played by the orientation of the molecules in the interface in determining the direction of curvature was suggested by Langmuir,[4] who said:

> This theory also affords an explanation of the mechanism by which colloids are formed. If a film of closely packed oleic acid molecules covers the surface of water to which sodium hydroxide has been added, OH groups are adsorbed by the COOH radicals, causing an expansion of the lower side. This results in the bulging of the film downwards in spots, so that it finally detaches itself in the form of particles, the outer surfaces of which consist of COOH groups together with the adsorbed OH, while the interior consists of the long hydrocarbon chains.
>
> The size of the colloidal particles is determined by the difference in size between the two ends of the molecules, just as the size of an arch is dependent upon the relative sizes of the two ends of the stones of which the arch is constructed.

Harkins, Davies, and Clark[5] have also expressed the opinion that the natural curvative of the film is determined by the orientation of the molecules in the interface. They say:

> It seemed to us that the only apparent relation was that to the number of oleate radicals in the molecule of the protective colloid (sodium oleate, or magnesium oleate). Therefore, it quite possibly may be the orientation and the form of the molecule, together with adsorbed ions in the interface between the dispersoid particles (or small drops) and the dispersion medium, which determine the surface energy relations, and, therefore, the size of the drop at which it becomes stable. In other words, this idea is that the drop would be stable whenever the molecules, together with adsorbed ions, etc., in the interface fit the curvature of the drop. The molecules in the curved surface would not need to be at all of the same kind. If the molecules do not fit in the curved surface, the drop will not be perfectly stable, and will either decrease or increase in size if given time.

It is possible to test the orientation hypothesis in a very striking way in the case of the soaps, where the work of Langmuir[4] of Harkins[5] and of Griffin[22] justifies the assumption that at an interface between water and some liquid of low polarity, such as

benzol, any soap would form an interfacial film, which might be as little as one molecule thick.

Now, if the polar group, in the water, occupies more space than is necessary for the closest packing of the hydrocarbon chain, the latter can be packed more closely if the film is convex on the water side. It is obvious that the direction and degree of curvature, if this hypothesis is correct, should vary, first, with the atomic volume, and, second, with the number of hydrocarbon chains attached to a single metallic atom, according to its valence. A zinc soap, for example, with two hydrocarbon chains per atom of metal, crowded together in the oil phase, should tend to make the film convex towards the oil, while an aluminum soap, with its three hydrocarbon chains in the oil, should give still more curvature towards the water and hence relatively stable emulsions of water in oil.

The relative sizes of the metallic atoms in the various soaps may be inferred from the atomic volumes of the metals, and from their atomic diameters in the free state and in compounds. Values are given in Table II. The atomic diameters are according to Hull,[16] Bragg,[17] and Richards,[18] respectively. Of course, hydration may modify the effective atomic domain, but since, for example, the hydration of silver ion can hardly be as great as that of sodium ion, this factor may be expected to increase rather than to oppose the effect of the differences evident in Table II.

Application of the theory to these figures would indicate that the ability of soaps of Ca, K, Na and Ag to emulsify oil in water would *decrease* in the order given; or, viewed from the other angle, their ability to emulsify water in oil should *increase* in this order; that the soaps of the divalent metals, Ca, Mg and Zn, should have much *less* ability to emulsify oil in water or much *greater* ability to emulsify water in oil, and, further, that they should vary in these respects in the order given. The soaps of the trivalent metals Al and Fe, should exhibit the greatest tendency to emulsify water in oil. The values in the several columns for the relative size of Fe and Al atoms do not all agree, so that the relative emulsifying powers are not definitely indicated by these figures. In general, the values for the atomic diameters of the free metals are most reliable, since the values for the atomic diameters in compounds involve two variables which require some further

consideration for their determination. On the other hand, there may be doubt that the elementary atom with its electrons occupies the same domain as does the atomic kernel in the compounds. However, there are enough uncertain factors involved to deter us from attempting to make any very fine distinctions on the basis of existing figures for atomic diameters.

TABLE II.—RELATIVE SIZES OF ATOMS

	Atomic diameters			Atomic volumes
	In metal	In halides		
	Hull	Bragg	Richards	
Ca	....	4.75	3.80	70.6
K	....	4.15	3.46 (in KCl)	45.3
Na	3.72	3.55	2.85 (in NaCl)	22.9
Ag	2.87	3.55	.....	10.3
Ca	3.93	3.40	.....	12.6
Mg	3.22	2.85	.....	7.0
Zn	2.67	2.65	.....	4.6
Al	2.86	2.70	.....	3.4
Fe	2.48	2.80	.....	2.3

There have been known for some time many facts which accord with this theory of the emulsifying powers of soaps. The soaps of the alkali metals are very effective in stabilizing oil in water emulsions, K soaps being more effective than Na soaps;[19] magnesium soaps emulsify water in oil;[20] salts of the trivalent metals, Al and Fe, are especially effective in reversing oil in water emulsions stabilized by soaps of the alkali metal.[21] Emulsions of oil in water stabilized by sodium oleate are reversed by adding magnesium, aluminum, ferrous, or ferric salts in amounts chemically equivalent to the sodium oleate used.[13]

Finkle, Draper, and Hildebrand have determined not only the type of emulsion but their relative stabilities, using stearates and oleates of the metals listed in Table II. The results obtained

for a typical series are shown in Table III, and are seen to be in close accord with the theory.

TABLE III

Oleate of	Dispersed phase	Approximate life of emulsion
Cs	Benzene	8 weeks
K	Benzene	8 weeks
Na	Benzene	6 weeks
Ca	Water	1 hour
Ag	Water	1 day
Mg	Water	2 days
Zn	Water	2+ days
Al	Water	7 days
Fe	Water	10 days

The results in these cases are also in accord with the rule that the external phase is the one which is the better solvent for the emulsifier. The soaps of the alkali metals are more soluble in water, the others more soluble in the non-polar liquid. The soaps of Fe and Al have more symmetrical and less polar molecules, and would, therefore, be expected to dissolve best in solvents of low polarity, while the alkali metal soaps, consisting of a single chain with a highly polar end, cannot dissolve considerably in non-polar liquids, but can, on the other hand, form clusters with the hydrocarbon chains in the interior, which can then dissolve "colloidally" in water.

If the orientation theory is correct, the different degrees of curvature natural to the films of different soaps should yield drops of different size. The authors just mentioned compared the drop sizes in emulsions of Na, K, and Cs soaps, respectively, and found the following sizes for the drops present in largest number in the three cases: Na soap, 0.005 mm.; K soap, 0.004 mm.; Cs soap, 0.0025 mm. The same relative order, though with different numerical values, was obtained in other series.

CRACKING OF EMULSIONS

The cracking of emulsions can be sought by destroying the conditions for stability. Thus, an emulsion of an oil in water

stabilized by the soap of an alkali metal can be cracked by adding the equivalent amount of heavy metal salt.[21] Water-in-oil emulsions can be treated by alkali soaps,[23] sodium carbonate,[24] sodium salts of sulfonated oils, and the like. Any reagent which destroys the emulsifier will also promote demulsification.

Electrical methods of demulsification are extensively employed and are effective, due to the effect of an electric charge upon the interfacial tension.[25] The relation between the charge on a sphere ϵ, its radius r, and the increase in surface tension due to the charge $\Delta\gamma$, is given by the equation:

$$\Delta\gamma = \frac{-\epsilon^2}{16\pi r}$$

Thus, if $\Delta\gamma = -20$ dynes, and $r = 10^{-4}$ cm., $\epsilon = 0.32$ c.g.s. units, or 95 volts. An electric field of sufficient magnitude, therefore, can exert enormous effects upon the surfaces of the droplets and destroy the stabilizing film.

REFERENCES

1. Rayleigh: *Proc. Roy. Soc.*, **47** (1890), 281.
2. Gibbs: *Scientific Papers*, **1** (1906), 219.
   For derivation of the quantitative relationship between adsorption, surface tension, and free energy, see Lewis and Randall: "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., 1923, p. 249. The present author has discussed this relation in connection with deviations from the ideal solution laws; Hildebrand: "Solubility," American Chemical Society Monograph Series (1924), Chap. XVIII.
3. Donnan: *Z. physik. Chem.*, **31** (1899), 42.
   Donnan and Potts: *Kolloid Z.*, **4** (1910), 208.
4. Langmuir: *Chem. Met. Eng.*, **15** (1916), 468; *J. Am. Chem. Soc.*, **39** (1917), 1848.
5. Harkins, Davies and Clark: *J. Am. Chem. Soc.*, **39** (1917), 354, 541.
6. Plateau: *Pogg. Ann.*, **141** (1870), 44.
7. Hillyer: *J. Am. Chem. Soc.*, **25** (1903), 513.
8. Holmes and Child: *J. Am. Chem. Soc.*, **42** (1920), 2049.
9. Ostwald: *Kolloid Z.*, **6** (1910), 103; **7** (1910), 64.
10. Pickering: *J. Am. Chem. Soc.*, **91** (1907), 2002.
11. Bancroft: *J. Phys. Chem.*, **16** (1912), 179.
12. Pickering: *J. Chem. Soc.*, **91** (1907), 2010; *Kolloid Z.*, **7** (1910), 11; Sheppard: *J. Phys. Chem.*, **23** (1919), 634; Schlaepfer: *J. Chem. Soc.*, **113** (1918), 522; Moore: *J. Am. Chem. Soc.*, **41** (1919), 940.
13. Finkle, Draper and Hildebrand: *J. Am. Chem. Soc.*, **45** (1923), 2780.

14. Clayton: "The Theory of Emulsions and Emulsification," P. Blakiston's Son and Co., 1923.
15. Adams: *Proc. Roy. Soc., London*, **99**A (1921), 336; **101**A (1922), 452. Griffin: *J. Am. Chem. Soc.*, **45** (1923), 1648.
16. Hull: *Proc. A. I. E. E.*, **38** (1919), 1171; *Science*, **52** (1921), 227.
17. Bragg: *Phil. Mag.*, 6, **40** (1920), 169.
18. Richards, T. W.: *J. Am. Chem. Soc.*, **45** (1923), 422.
19. Neunier and Maury: *Collegium* (1910), 277; *Chem. Zentr.* (1910), II, 1416.
20. Newman: *J. Phys. Chem.*, **18** (1914), 34.
21. Bhatnagar: *J. Am. Chem. Soc.*, **119** (1921), 61, 1760.
22. Griffin: *J. Am. Chem. Soc.*, **45** (1923), 1648.
23. Parsons and Wilson: *J. Ind. Eng. Chem.*, **13** (1921), 1116.
24. Matthews and Crosby: *J. Phys. Chem.*, **20** (1916), 407.
25. *Cf.* Eddy, W. G. and H. C.: *J. Ind. Eng. Chem.*, **13** (1921), 1016.

CHAPTER VIII

EMULSIONS AND FOAMS*

By

Harry N. Holmes

Emulsions are dispersions of one liquid in another liquid. Strictly speaking, the drops or globules should be of colloidal dimensions, yet much coarser dispersions are often included in the term *emulsions.* Two mutually insoluble liquids may be shaken, beaten, or ground together to form emulsions, but they soon separate into two layers of the original liquids. Such emulsions are stable only if the dispersed phase does not exceed 1 or 2 per cent of the total volume. Condensed water from an engine often carries an extremely small amount of lubricating oil thoroughly emulsified.

To prepare a similar emulsion, one may pour 10 cc. of a 1 per cent solution of any suitable oil in acetone (or alcohol) into 1,000 cc. of water. The author has at hand a comparatively stable emulsion of this type prepared nine years ago. Distillations from mixtures often produce annoying emulsions.

The stability of these extremely dilute emulsions of "oil in water" is probably due very largely to the negative charge, of the order of 0.05 volts (Lewis[1]), carried by the drops. In this respect they resemble suspensions of solids in liquid. There may be resemblance in another respect, too. When drops are sufficiently small, surface forces give them the rigidity of solids. In this connection it might be remarked that if one melted a solid fat and dispersed it in hot water, an emulsion would result, but, on sufficient cooling, this emulsion would change to a suspension of a solid in a liquid.

*Some of the material in this chapter was taken, by permission of John Wiley & Sons, Inc., from the Laboratory Manual of Colloid Chemistry by the Author.

With the exception indicated above, stable emulsions of two pure liquids cannot be prepared. A third substance, usually colloidal, is necessary to stabilize emulsions. This is often present as an unsuspected impurity, or it may be added purposely. The exact manner in which the *emulsifying agent* functions is still disputed. The various theories are presented in the following section.

Emulsion Theories

Quincke,[2] and later Donnan and Potts,[3] held that interfacial tension lowering was a very important factor in stabilizing emulsions. This view receives much experimental support. The alkaline soaps are, perhaps, the most commonly used emulsifying agents and, as a class, they produce marked lowering of the surface tension of water. Donnan and Potts showed that noticeable emulsifying power and surface tension lowering in the fatty acid series begins with the alkaline laurates. These two properties become more marked with increase in molecular weight, as do colloid properties in general.

Water has a high surface tension, which naturally tends to pull all the water of an emulsion into one large drop, or layer, in order to expose the least possible surface. Any substance that lowers this tension must weaken this layering tendency, and thus stabilize an emulsion.

The most generally accepted theory is the adsorption film theory advanced by Bancroft.[4] This is founded upon Gibb's statement that any substance which lowers the surface tension of a liquid must concentrate at surfaces or interfaces. By such concentration, a film forms around each drop, thus interfering with coalescence of drops and breaking of the emulsion Hillyer,[5] in his classic discussion of soaps as emulsifying agents, stresses the primary importance of low interfacial tension as well as the high superficial viscosity of certain emulsion films. Bancroft considers that the best film should be tough and elastic. R. E. Wilson[6] holds that it is really a plastic solid.

Briggs[7] insists that if the emulsifying agent is peptized too well by the continuous phase the adsorption film will not be formed; consequently, addition of a mild flocculating agent must

be helpful in some instances. Thus a 1 per cent solution of hydrous ferric oxide was found to be a poor emulsifying agent, while addition of 1 g. of pure sodium chloride to 40 cc. of this solution made possible a coarse dispersion of 10 cc. of benzene in the solution. A higher concentration of salt increased the stability of the emulsion. Sodium sulfate, however, was too strong a coagulant, precipitating the ferric hydroxide in coarse flocks.

The author has observed that if large drops of water are allowed to flow slowly from a pipette into a 2 per cent solution of gum dammar, visible adsorption films form in a fraction of a minute. When these large drops are rolled around, the films wrinkle and show some toughness and elasticity.

The following is quoted from a pamphlet issued by the Sharples Specialty Company.

> When crude corn oil is agitated with hot water, a thick, white emulsion forms. When this emulsion is passed through the Sharples Super-Centrifuge at a moderate rate of flow, some of the oil separates and is discharged in a highly emulsified condition.
>
> The oil separated in this way will not form a stable emulsion when again agitated with hot water, because the emulsifying agent has been extracted. But, when the discharged emulsion is broken by any chemical means, the separated oil is easily emulsified again.

This indicates a concentration of the emulsifying agent at the oil-water interface. Briggs[8] observed a removal of soap by the cream from an emulsion—another indication of concentration at interfaces. Martin Fischer and Hooker[9] believe that, in general, highly hydrated colloids are the best emulsifying agents, because they "bind" all the water. If more water is present than can be bound by the colloid, the emulsion is not stable. As support for this hydration theory, they instance the good emulsifying properties of such hydrated colloids as the alkali soaps, gelatin, gum arabic, albumin, and acid casein (or alkali casein). Neutral casein is a poor emulsifying agent, because only slightly hydrated, while either acid casein or alkali casein is highly hydrated and a good emulsifying agent.

Fischer also instances mayonnaise as an example of the use of a hydrated colloid as emulsifying agent. The hydrated proteins

of the yolk function here. In fact, egg yolk itself is an emulsion of over 30 per cent fat in hydrated proteins.

Pickering[10] prepared very good emulsions of oil in water by the use of a finely divided basic ferrous sulfate, freshly precipitated, as emulsifying agent. Basic cupric sulfate served as well. This is startling, because any films surrounding the oil drops were composed of small discrete solid particles, probably non-crystalline. Pickering concluded that all emulsion films had a similar structure and gave surface tension a minor rank. In this he went too far. Pickering's[11] name is always associated in emulsion history with his 99 per cent oil emulsion with soap water as the continuous phase.

Harkins, Davies, and Clark[12] think that the best emulsifying agents have long molecules with a polar active group at one end of the molecule (polar groups such as –COOH, $-SO_3H$, and –COOR). Langmuir[13] believes that the hydrocarbon part of the molecule strikes inward into the fatty globules, while the –COOH, $-SO_3H$, and similar groups are outside in the water phase. This orientation theory is quite evidently applicable to the soaps, but certainly does not apply to Pickering's emulsions.

The author regards an interfacial film as an equilibrium product resulting from the peptizing action on the one side and the precipitating action on the other. If the film material be swollen with liquid on one side, it will be more elastic. Hildebrand offers the suggestion that the volume of one or the other end of a long molecule (such as a soap) really determines whether the surface shall be convex or concave toward a given liquid—in other words, determines whether the oil or water shall be the dispersed phase. Harkins, Davies, and Clark offered a somewhat similar suggestion a few years earlier. They contended that in a calcium soap, for example, the two oleate radicals (or stearate, etc.) in the soap chain produced a wedge shape just the opposite of the shape of the sodium oleate chain. Hence, the inversion in type.

Two Types of Emulsions

The more common emulsions are dispersions of "oil in water." By "oil" is meant any liquid not miscible with water. In 1910, Wo. Ostwald first drew general attention to another type, "water-

in-oil" emulsions, in which oil is the continuous phase and water the dispersed drops.

The determination of which liquid is to form the dispersed phase depends upon the choice of the emulsifying agent. Alkali soaps always give emulsions of the usual oil-in-water type, while heavy metal soaps yield the less usual water-in-oil type. It is significant that alkali soaps are soluble in, or peptized by, water and are usually far less soluble in the other liquid. Heavy metal soaps are usually less soluble in water than in the other liquid chosen.

Out of such observations came a general rule. If the emulsifying agent is more readily peptized or even more readily wetted by water than by oil, the oil-in-water type of emulsion results, but if the emulsifying agent is more readily peptized or wetted by oil than by water, the water-in-oil type of emulsion results.

Schlaepfer[14] was able to disperse 70 per cent (by volume) of water in 30 per cent of kerosene, using soot as the emulsifying agent, because the soot was more readily wetted by oil than by water. W. E. Moore[15] did the same thing, using carbon, oil, and aqueous solutions of ammonium chloride.

Clowes[16] considers that the determination of phase depends upon the convex or concave bending of the liquid interface as influenced by surface tension lowering, caused by the emulsifying agent. He added a calcium salt to an emulsion of oil in water stabilized by sodium oleate and changed the type. Of course, a calcium soap was formed by double decomposition, and it favored formation of a water-in-oil emulsion. Clowes states that when the equivalent ratios of Ca: Na were 1 :4, the opposing effects were balanced and neither type was formed. Clowes holds that the adsorption of Ca ions or Na ions by the film is a vital factor in determination of phase.

Bhatnagar[17] goes so far as to say that:

> All emulsifying agents having an excess of negative ions on them and wetted by water will yield oil-in-water emulsions, while those having an excess of adsorbed positive ions and wetted by oil will give water-in-oil emulsions.

Clayton,[18] in his invaluable book on "The Theory of Emulsions," expresses the belief that "before much further advance

can be made towards a general theory of emulsions attention must be paid to the wetting of various emulsifiers by different liquids," and that the important physical factor to be studied is that of the angle of contact between liquid and solid.

The relative volumes and order of addition of the two liquids in an emulsion have some influence on the type. Clayton[19] in reporting on the manufacture of margarine remarks that, if oil is slowly fed into milk in bulk, with agitation, a stable oil-in-water emulsion results; but if milk is fed very slowly into oil in bulk, a very unstable system of water in oil results.

The use of finely divided solids as emulsifying agents has been studied very thoroughly by Bechold, Dede, and Reiner.[20]

Holmes and Cameron[21] found gum dammar, in many respects, the best emulsifying agent for the preparation of the water-in-oil type of emulsion. They also found cellulose nitrate, peptized by such solvents as amyl acetate, very useful in dispersing water or glycerol.

A partial list of the two types of emulsifying agents follows. Of course, a great many more might be added if desired.

EMULSIFYING AGENTS

For oil-in-water emulsions:	For water-in-oil emulsions:
Sodium oleate	Gum dammar
Other alkali soaps	Calcium oleate
Gelatin	Other heavy metal soaps
Saponin	Lanolin
Albumin	Rosin
Lecithin	Rubber
Casein (acid or alkaline)	Cellulose nitrate

HOW TO RECOGNIZE EMULSION TYPES

The drop-dilution method of testing emulsions, as described by Briggs,[22] is the most generally useful. A drop of the emulsion in question is placed upon "water." If it mixes readily with the water, the emulsion is a dispersion of oil in water. If placed upon "oil," such a drop would not spread readily because the oil drops in the emulsion would be separated from the bulk oil by the surrounding phase, water. The other type of emulsion would act in the opposite way. In general, when the drop mixes readily the continuous phase is the same as the bulk liquid.

The dye-spreading method of Robertson[23] is often useful. A few minute particles of an oil-soluble dye (such as Sudan III) are sifted over the emulsion. If the color spreads, oil must be the continuous phase. If oil were dispersed, it is obvious that the dye could not jump from drop to drop.

The differences in conductivity for heat and electricity are evident when the continuous phase is oil and when it is water. Differences in the splash sounds when the two types of emulsion are shaken in a bottle may also be used in recognizing type.

Making and Breaking Emulsions

Of course, the emulsifying agent must first be dispersed in the liquid to be made the continuous phase. It is the general rule that the liquid to be dispersed should be added slowly with constant agitation. Briggs, however, believes in the superior merit of intermittent shaking. Grinding is favored by pharmacists who often desire to make very viscous emulsions. Martin Fischer[24] advocated a rotating cone which could be forced very close to a casing, so that a smearing action could tear globules into smaller drops. This principle is used in the Premier Mill now being placed on the market. Briggs'[25] homogenizer is a simple but effective laboratory device.

The housewife is familiar with the use of an egg beater in whipping up a mayonnaise. Quite as simple in principle is shaking by hand or by machine. In this case additions of oil or water must be intermittent. There is need for a method of removing the emulsified drops as fast as formed, suggests Clayton. The increase in viscosity with increasing richness of an emulsion interferes with free splashing and smashing of the liquid to be dispersed. The volume of free air in the splash bottle may affect the method of shaking, due to concentration of the emulsifying agent at bubble surfaces.

In breaking an emulsion the important thing is to change the emulsifying agent chemically or physically so that it is no longer effective. Adding an acid to an emulsion stabilized by sodium oleate changes the agent into oleic acid, which has no emulsifying properties. Emulsions are least stable when brought near the inversion point, that is, near the point at which they change type.

Addition of an emulsifying agent of opposite type is often effective in breaking. Thus, a calcium soap antagonizes a sodium soap. Sometimes addition of the dispersed liquid in bulk has a breaking effect. Coalescence of drops is often secured by the addition of polyvalent ions opposite in charge to the drops. Coalescence by passage of an electric current was patented by Cottrell[26] with a view to removing the objectionable water drops from certain petroleums. Some emulsions can be "salted out." This may mean the dehydration of the swollen films. The centrifuge not only separates creams, but in some cases breaks emulsions. Heating under pressure has been known to break certain petroleum emulsions. The emulsifying agent in oil field emulsions (water in oil) is generally an asphaltic material. Phenol, soluble in both oil and water, has been used to carry hydrogen ions into the water drops, thus neutralizing the negative charge on the drops. A mineral acid, soluble in water, tends to break emulsions of oil-in-water, while some organic acid, soluble in oil, tends to break water-in-oil emulsions.

Creaming

Cream rises to the top in milk because the fat globules are lighter than the watery portion of milk. The centrifuge accentuates this gravity difference and so is used as a cream separator. The larger drops rise more readily than smaller ones. This difference is carried to the extreme in homogenized milk which never creams. The fat globules have been reduced to one-tenth their usual size.

It is evident that when the dispersed phase is heavier than the continuous phase, the cream will sink. An emulsion of carbon tetrachloride dispersed in water by sodium oleate creams upwards, while an emulsion of carbon tetrachloride dispersed in water by gum dammar creams downwards.

The obvious inference is that an emulsion made up of two phases of the same density will not cream. This is true to a degree. Temperature changes affect the densities of the two liquids differently, however, and the original condition might not continue.

Transparent and Chromatic Emulsions

Usually, when two transparent liquids are emulsified, a milky-white mixture results. Olive oil shaken with water illustrates this; yet transparent emulsions can readily be prepared. Transparency depends upon the relative indices of refraction of the two liquid phases. If both phases have the same index, there will be neither reflection nor refraction, and the system will appear homogeneous and entirely transparent. Glycerol dispersed in a 2 per cent solution of calcium oleate in carbon tetrachloride yields a fairly transparent emulsion. Gum dammar could be substituted for the calcium oleate.

Holmes and Cameron[27] dispersed glycerol in amyl acetate containing about 2 per cent of cellulose nitrate (11.04 per cent nitrogen). The emulsion was milky in appearance. They then gradually added, with shaking, a considerable volume of carbon disulfide, and the emulsion became nearly transparent. The explanation is simple enough. Carbon disulfide dissolved in the continuous phase, amyl acetate, and raised its index of refraction to equality with that of the glycerol. On further addition of carbon disulfide, beautiful color changes appeared. The whole chromatic scale of colors was brought out and was reversed by additions of amyl acetate, which, of course, lowered the index of refraction of the continuous phase. Benzol may be substituted for the carbon disulfide, although the results are not so striking, rubber for the cellulose nitrate, and water solutions for the glycerol.

To secure such structural colors (a sort of Christiansen effect), it is necessary to have two mutually soluble liquids for the continuous phase, one of high refractive index and high optical dispersive power (as a prism disperses light). Carbon disulfide, benzene, and a concentrated aqueous solution of potassium iodide supply high optical dispersive power. Size of drops has little to do with the phenomenon. The gradual change in optical dispersive power is vital.

Froth and Foam

There is a close resemblance between emulsions and foam. The one is a dispersion of liquid in liquid and the other a disper-

sion of gas in liquid. Adsorption films act as emulsifying agents, and absorption films may surround the gas bubbles in foam.

Miss Benson[28] first demonstrated that a froth of aqueous amyl alcohol showed a higher concentration than did the solution beneath. Kenrick[29] shook 0.08 g. of methyl violet in 300 cc. of water and secured a good froth. After removing this froth he broke it with a drop of ether, and, by color comparisons after diluting with water, he proved that the dye had concentrated in the froth films. Adsorption at a liquid-gas interface is the same sort of thing as adsorption at a liquid-liquid interface.

The saponins are remarkable frothers, better even than the alkali soaps. These soaps lower surface tension and so concentrate at interfaces, but the saponins do not lower surface tension greatly. Their frothing power is due largely to the high superficial viscosity of saponin films. To use R. E. Wilson's phrase, these films are "plastic solids."

Flotation froths are of this type. Pulverized sulfide ores, for example, are beaten in water carrying a little oil. Since the gangue is preferentially wetted by water, this portion of the ore sinks, while the valuable sulfide, being preferentially wetted by oil, attaches itself to the oily froth and "floats." The very temporary froth is given a high superficial viscosity by the finely ground sulfide and is thus stabilized. Of course, the froth is removed, broken by jets of water, and the sulfide recovered.

A famous fire-extinguishing mixture contains soda and alum to furnish carbon dioxide, and an extract of licorice to give stability to the foam. Bancroft, in his "Applied Colloid Chemistry," calls attention to the fact that violent shaking of a rennet solution destroys most of its power to coagulate milk. The enzyme concentrates in the froth. On the other hand, shaking does not inactivate a rennet solution carrying some saponin, because the latter is preferentially adsorbed at the interfaces and thus keeps the rennet from being coagulated.

Salts cause foaming (or "priming") in boiler water, but not because the surface tension is lowered. Bancroft[30] insists that either increase or decrease in surface tension is sufficient to cause foaming.

REFERENCES

1. *Kolloid-Z.*, **4** (1909), 211.
2. *Ann. (Pogg.)*, **139** (1870), 1–89; *Ann. (Wied.)*, **35** (1888), 571–580.
3. *Kolloid-Z.*, **7** (1910), 208–214.
4. *J. Phys. Chem.*, **17** (1913), 514–18; *J. Phys. Chem.*, **19** (1915), 275.
5. *J. Am. Chem. Soc.*, **25** (1903), 513.
6. *Chem. Met. Eng.*, **24** (1921), 825.
7. *J. Ind. Eng. Chem.*, **13** (1921), 1008.
8. *J. Phys. Chem.*, **19** (1915), 210.
9. *Kolloid-Z.*, **18** (1910), 129; "Fats and Fatty Degeneration," John Wiley & Sons, New York, 1917.
10. *Kolloid-Z.*, **7** (1910), 11–16; *J. Chem. Soc.*, **91** (1907), 2010.
11. *J. Chem. Soc.*, **91** (1907), 2002.
12. *J. Am. Chem. Soc.*, **39** (1917), 541–596
13. *J. Am. Chem. Soc.*, **34** (1917), 1848.
14. *J. Chem. Soc.*, **113** (1918), 522.
15. *J. Am. Chem. Soc.*, **41** (1919), 940.
16. *J. Phys. Chem.*, **20** (1916), 407–451.
17. *J. Chem. Soc.*, **120** (1921), 1768.
18. "The Theory of Emulsions," Blakiston's Son & Co., Philadelphia, 1923.
19. *J. Soc. Chem. Ind.*, **36** (1917), 1205.
20. *Kolloid-Z.*, **28** (1921), 6–19.
21. U. S. Pat. 1429430 (1922).
22. *J. Phys. Chem.*, **18** (1914), 34.
23. *Kolloid-Z.*, **7** (1910), 7–10.
24. "Fats and Fatty Degeneration," John Wiley & Sons, 1917.
25. *J. Phys. Chem.*, **19** (1915), 223.
26. U. S. Pat. 287115 (1911).
27. *J. Am. Chem. Soc.*, **44** (1922), 71.
28. *J. Phys. Chem.*, **7** (1903), 532.
29. *J. Phys. Chem.*, **16** (1912), 517.
30. "Applied Colloid Chemistry," McGraw-Hill Book Co., 1921.

CHAPTER IX

ADSORPTION IN COLLOID SYSTEMS

By

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In the classical development of the phase rule the phenomenon is, in general, ignored that the surfaces of the phases may have different composition from the main portion of the phase, notwithstanding the existence of chemical equilibrium. Complete homogeneity within each phase is a necessary assumption in order to define it as a true phase. This definition requires that each phase has a uniform composition even to the very point of contact with the second phase. It is with the correction of this wrong assumption that the phenomenon of adsorption is chiefly concerned. The necessity for this correction was clearly recognized and expressly formulated by Willard Gibbs,[1] the originator of the phase rule. Quite independently, though at a later date, J. J. Thomson[2] deduced the same relation. The Gibbs theorem is stated

$$\mu = c \cdot \frac{d\sigma}{dc} \cdot \frac{dc}{dP}$$

where μ is the excess in concentration, in the boundary layer, of a substance dissolved in a phase or present in the gaseous form over and above its concentration c within the phase. The upper limit of concentration is thus $c + \mu$. Further, σ is the surface tension of the boundary layer and P the osmotic pressure of the solute (or alternatively the gas pressure). If one accepts the validity of van't Hoff's law for dilute solutions, then

$$\frac{dc}{dP} = \frac{1}{RT}$$

where R is the gas constant and T the absolute temperature, and the former equation may be written

$$\mu = -\frac{c}{RT} \cdot \frac{d\sigma}{dc}$$

If $\frac{d\sigma}{dc}$ is negative, that is, if the dissolved substance lowers the surface tension of the solvent, and, indeed, the higher the concentration the greater the lowering, the adsorption becomes positive, and the solute is in higher concentration in the surface layer. The alcohols, esters, and many other organic non-electrolytes in aqueous solution are in this sense *surface active* or *capillary active* substances. It also appears to be true that, within an homologous series of similarly constituted substances, the surface activity increases rapidly with each increase in the carbon chain, as was stated by Traube. Such substances are, therefore, a suitable starting point in the study of adsorption.

The theorem of Gibbs is based on thermodynamics and cannot, indeed, be questioned. But we may ask what can be accomplished with it, whether we are in a position to draw conclusions from it which experiment can confirm, and what degree of accuracy we may expect from it.

The Practical Significance of the Gibbs Theorem

In the first place, can one evolve a definition of adsorption by original reasoning from the Gibbs theorem? We may understand by adsorption the phenomenon that takes place when an enrichment of a dissolved substance in the surface layer is to be found. The enriched substance we may call the *adsorbate* (after Taylor) or the adsorbed phase; the other phase the *adsorbent* or the adsorber. This definition is useful, but it leads to a peculiar consequence. Thus, when a solution borders a vacuum, or, more exactly, when it borders its vapor (for equilibrium is demanded) which, in comparison with the liquid phase, has almost no mass, the surface of the solution enriches itself with a capillary active substance, as is required by the Gibbs theorem. In this case the vacuum is the adsorbent. This somewhat strange deduction from the definition can be accepted, as it is based on a purely formal definition. Should it become desirable in some special case to differentiate, this could be designated as *apparent adsorption*[3] in contradistinction to *true adsorption*. Gibbs' theory may, of course, be considered only as a law holding under ideal conditions

and one which is realized experimentally in few cases. Adsorption is measured at the concentration μ, which refers only to the outer limiting surface. The concentration of the limiting surface does not, however, necessarily fall suddenly to that of the remaining solution, but sometimes gradually, even though the concentration gradient is steep. Analytically, however, we cannot determine the concentration of the limiting layer, but only the total loss produced in the solution by adsorption. In the case of a monomolecular adsorption layer, the conception of the "concentration" of the surface layer becomes still more doubtful. The factor μ is further represented as a function of quantities which we can only partially measure. T and R are, indeed, simple, but the determination of the magnitude of the surface tension presents the greatest difficulties. We can measure the surface tension only against air or, in special cases, against a second liquid immiscible with the first; unfortunately, therefore, only in such cases as are not adapted to analytical adsorption experiments. The surface tension of a liquid against a solid adsorbent which may be used in powdered form, as charcoal, is not measurable. The only method by which one may determine qualitatively whether a substance dissolved in water lowers the surface tension against charcoal is merely the investigation of its ability to adsorb this substance. Experience teaches us naturally that, in a series of cases, surface activity proceeds parallel to adsorption by a solid adsorbent (Freundlich's rule).[4] Thus, for example, the alcohols or esters of an homologous series are increasingly better adsorbed by charcoal in the same degree as their surface tension against air becomes greater.

But there are many exceptions to this rule. In the first place there are substances which increase the surface tension of water against air and still are adsorbed by charcoal (sugar). In the second place, this parallelism, so far as it exists, is manifest only in the case of adsorption by charcoal. Thus, for example, there is no surface-active non-electrolyte which is adsorbed in the slightest degree by kaolin or by ferric hydroxide.[5] In these cases the surface tension against air is no criterion for the surface tension against the adsorbent. Either Gibbs' theory fails, which one is unwilling to conclude, or, at least, it offers nothing to the solution of the problem.

Difficulties of the Concept of Surface Tension and Adsorption

One reason why the parallelism of the surface tension against air and against a solid adsorbent is lost is doubtless the formation of electrical charges on the surfaces. Every electric charge must affect the surface tension. We may divide the total tension into two components: the purely mechanical tension, which causes the usual adhesion and cohesion in the absence of free electrical charges, and an electrically negative tension or expansion effect, due to the covering of the surface with electric charges of like sign. This is shown by the fact that the pressure within a soap bubble, as measured by a manometer, diminishes when it is electrified. In Gibbs' formula σ can only be the total tension. It is noteworthy that Gibbs' theory becomes inapplicable when the substance is of a decided electronegative or electropositive character, while for indifferent materials such as charcoal it is moderately applicable. However, these relations are not yet clear, since charcoal also has, in general, an electrical potential difference against the solution.

For mechanical surface tension we may draw the following picture. A molecule of a liquid is attracted equally by the neighboring molecules on all sides, and is held, therefore, under an internal pressure. A molecule lying on the surface occupies a unique position because the resultant of all the molecular attractions is not zero. This results in a surface tension. But we may also use molecular attraction as the starting point of our consideration of adsorption. The qualitative content of Gibbs' theorem would be: "A substance dissolved in water is adsorbed at the surface of another substance when its adhesion to the second substance is greater than its cohesion for its own phase." This proposition is only a self-evident paraphrase. If one expresses in this way the relation so frequently quoted between surface activity and adsorption, the whole inadequacy of it will be apparent. All that remains of this oft-cited relation can be summed up as follows: If the adsorbent is charcoal and the adsorbate an organic non-electrolyte (or a weak electrolyte), it is generally true, although not without exceptions, that the ability of a substance to be adsorbed is parallel to its surface activity against air.

It is worthy of note that useful conceptions of adsorption have not resulted from the thermodynamic proposition of Gibbs, but have resulted by taking as a basis the force of molecular attraction. Polanyi's theory of adsorption and also the well-known investigations of Harkins and Langmuir have so arisen, but cannot be discussed at this place.

Molecular attraction of every degree exists between that of distinct chemical combination and that of the loosest adhesion. Formerly we distinguished sharply between chemical and physical combination. Today it is no longer expedient to lay great stress upon this difference or to differentiate the adsorption phenomenon from a chemical reaction. Otherwise we will be faced with the embarrassment of being compelled to designate as adsorption the attraction of methylene blue by charcoal, and as no adsorption the attraction of methylene blue by kaolin. Furthermore, in the case of charcoal we will be completely at a loss to establish a chemical equation for the process, while with kaolin a true substitution of calcium and similar ions* for methylene blue ions has been proved. This is surely a reaction which is generally accepted as chemical. At the same time it is not permissible to exclude the combination of methylene blue and kaolin from the group of processes known as adsorption. Numerous investigations are described in the literature where an attempt is made to demonstrate a difference between chemical combination and adsorption. Thus, Bayliss[6] describes the following experiment. If we shake the colloidal blue solution of Congo red acid with aluminum hydroxide, there results immediately a blue adsorption compound, and only gradually is the red aluminum salt of the Congo red acid produced.

It may be remarked that intermediate steps occur also with other chemical reactions, in which no doubt is entertained of the chemical character of the first step. Haller[7] writes that the precipitates which result upon mixing basic and acid dyes of high molecular weight do not show the stoichiometric composition which would be expected of a salt of an acid and a basic dye, and that the composition of the precipitate is variable. However,

* Although kaolin is an aluminum silicate, it appears that under these circumstances calcium, present as an impurity, is always displaced more than aluminum.

since such dyes tend to form colloidal micelles it is, indeed, quite possible that the micelles of one dye combine with the molecules of the other only at the surface. Such a compound cannot, of course, have a constant composition. Willstaetter[8] points out that wool, an optically active compound, adsorbs racemic alkaloids, but without any preference for the optically active component, which, however, would be expected in the formation of a true salt. This indicates without doubt that the compound formed by adsorption is not similar to a salt which may be prepared in a crystalline condition. It apparently behaves as a loose preliminary of true salt formation, but that this does not result from a chemical attraction may not be proved by this experiment. It is assuredly true and worthy of note that, with reactions taking place only at the surface, just such loose compounds are preferred.

The following conception of Haber[27] is most important. In a crystal the molecules are held together by the forces of valence and, in general, these are satisfied. But the molecules lying on the surface are not completely saturated and the residual valences of the surface represent the field of adsorption possibilities. With amorphous substances such residual valences may be exaggerated. This theory explains the case where reciprocal adsorption is not manifest. But with reciprocal adsorption the main valences are effective. All this emphasizes a gradual transition, and it is, therefore, not advantageous to regard an adsorption as a condition essentially different from that of a chemical reaction. To us, adsorption should signify chemical combination if it takes place at the surface of a substance and limits itself to the surface. But even with this definition we meet with transition cases. The example of permutite[9] places us again in error. This amorphous insoluble silicate, according to Schulze,[10] exchanges its total content of sodium for calcium, and *vice versa.* The active surface extends so far inward, perhaps by capillary fissures, that every molecule can enter the reaction. There is here no longer any difference between molecules on the surface and those in the interior, and the surface reaction becomes a complete chemical reaction. All compounds formed at the interface between the dispersed phase of a colloidal solution and the dispersion medium, either with or without reciprocal adsorption, must in any event

be attributed to adsorption phenomena, and this chapter on "Adsorption in Colloid Systems" could, on this ground, be equally well entitled "The Chemical Reactions of Colloidal Substances." It is evident that such a chapter can present only general points, for the special part of this chapter is at least half of the entire theory of colloids.

The Significance of the Surface-active Non-electrolytes for the Colloid State

The stability of a colloidal solution is determined at any given moment by the surface tension between the disperse phase and the dispersion medium. A continued rise of this tension must lead to coagulation. As one, in general, would expect that surface-active non-electrolytes, like alcohols or esters, should rapidly lower the surface tension, so also would it be expected that these substances should act as stabilizing agents upon colloidal solutions, *e.g.*, that with their help it should be quite possible to bring other substances into colloidal aqueous solution. With these materials it would be anticipated that this property should maintain even in extremely dilute solution, since one always attributes a much higher concentration to the surface layer. In reality, however, any action of these substances on the colloidal condition is very slight, and where it is at all present coagulation is nearly always favored rather than stabilization. In order to explain at all this slight activity we must call to mind once more the fact, often little appreciated, that all of these so-called surface-active substances reduce the surface tension of water only against air, water vapor and charcoal, but not, in general, against all surfaces.

The most surface-active substances, such as heptyl and octyl alcohols, fatty acid esters, and higher urethanes, are not in the slightest degree adsorbed by such substances as kaolin, alumina, ferric hydroxide, or, indeed, by most other inorganic materials, even though the adsorbent be brought into the finest state of subdivision. Thus, a sol of ferric hydroxide with its particles the size of amicrons, in the highest possible concentration, adsorbs no trace of octyl alcohol, etc., as was shown by Michaelis and

Rona[5] with the aid of a compensation dialysis. Adsorption was only in an extremely low degree demonstrable, even under most favorable conditions, with several other substances, such as talc, cellulose (filter paper), and sulfur. It was best with sulfur, while for such traces of adsorption as occurred with talc or filter paper there is present the objection that the slightest contamination of the surface with fats would vitiate the observations.

Except in the presence of electrolytes, the non-electrolytes are generally without influence upon the condition of the colloid and it is, therefore, a matter of indifference whether the non-electrolyte is surface-active or not. From numerous observations may be mentioned the finding of Freundlich[11] that methyl and ethyl alcohols, urea, cane sugar, and phenol, even at high concentrations, are without action upon arsenic sulfide sol, and, according to Wo. Ostwald,[12] the same is true of the very dissimilar Congo red sol. With non-electrolytes which are miscible with water in all proportions, as ethyl alcohol, it must be remembered that at high concentrations it is no longer an aqueous solution, and the fact that finally an aqueous sol can be precipitated by ethyl alcohol is certainly not a matter of concern in a chapter on adsorption. Moreover, the strong surface-active non-electrolytes are all so difficultly soluble that a like condition does not then come into question. The essential property which concerns us in this phenomenon is, indeed, the dielectric constant of the solvent, and this is but little altered by strong capillary-active substances because of the too slight solubility, although in the pure state their dielectric constants are much smaller than that of water.

The situation is different when such water-insoluble substances as the higher alcohols, benzol, or oils are shaken in undissolved condition with any substance in colloidal solution. When the emulsion of this oil produced by shaking separates, it often carries down the colloid also. This is as true for the protein type of solutions as for the suspension colloids. Here the dissolved colloidal material acts not as an adsorbate but as an adsorbent. The phenomenon was investigated by Zsigmondy[13] for gold sol. This is, in general, coagulated by shaking with benzine, carbon disulfide, etc., the gold separating as a shiny membrane at the interface of the liquids. The phenomenon does not persist

when the gold particles are very small. However, these cases do not belong here.

In the presence also of electrolytes, surface-active substances in the dissolved state often show a sensitizing action upon a colloid. The quantity of electrolyte just necessary for coagulation is decreased through its presence. Freundlich and Rona[14] found that the coagulating concentration of sodium chloride upon a ferric hydroxide sol was reduced, by the addition of 10 millimols of camphor per liter, from 35 to 27 millimols of sodium chloride per liter or, by the addition of 5 millimols of thymol, to 20 millimols. The action of these substances increases rapidly in homologous series, as does the surface tension, according to the rule of Traube. Closely related to this is the observation of Rona and Györgyi[15] that the settling of kaolin suspensions is accelerated by the addition of camphor, thymol, or tributyrin. It is extraordinary that this action is not observed in the settling of charcoal suspensions. Thus, there is no action with those powders which adsorb these substances while there is an action with those which do not adsorb them. There seems to the writer to be no satisfactory explanation yet advanced for this phenomenon. Freundlich thinks that the change in the dielectric constant of the water is the essential factor. But, in order to admit a change in dielectric constant, one must also assume that these substances become more concentrated on the surface, for, in the concentration in which they usually exist in aqueous solution, these constants do not materially change.

Experience shows, however, that these substances do not become concentrated on the surfaces toward which they are active. One might, therefore, believe that the surface-active substances influence the adsorption of the electrolyte in some way, and, through this, change the potential of the surface. But in such cases as are at all approachable by chemical analysis, Lachs and Michaelis[30] showed that an opposing influence of electrolyte and non-electrolyte as regards adsorption does not take place at all, and the divergences from this principle which have been found are quite insignificant and apparently limited to special conditions. One case in point may be found desirable for further investigation. According to Freundlich and Rona, sensitization takes place only with monovalent, difficultly adsorbed

ions, and not with divalent and better adsorbed ions. Thus, camphor sensitizes the action of sodium chloride, but not that of calcium chloride upon ferric hydroxide sol. They explain this as follows:[4(p. 638)] Coagulation begins as soon as a determined amount of cations is adsorbed, and this minimum amount is reduced by the addition of non-electrolytes. When, now, the quantity of adsorbed ions is reduced to a certain value, so also must the concentration containing an equal amount of ions in solution be reduced to a determined value. With the monovalent ions which are little adsorbed and have a flat adsorption curve, this amount is noticeably large. On the other hand, with the bivalent ions showing a steeper adsorption curve, it is very small.

Entirely unexplained, however, is the observation of Kruyt and van Duin[16] that the coagulation of arsenic sulfide sols by amyl alcohol, phenol, etc. is sensitized by the addition of mono and trivalent ions but, on the other hand, is weakened by the addition of di and tetravalent ions.

The Adsorption of Electrolytes

In contrast to the little-investigated and slight action of the non-electrolytes on colloids is the well-known behavior of electrolytes. The addition of an electrolyte is the method most generally used for intentionally altering the nature of a colloid. This action is intimately concerned with adsorption, for all the surfaces, which behave indifferently towards non-electrolytes, have the ability to adsorb electrolytes in large measure. This adsorption of the electrolyte takes place in a manner which is dependent on the nature of the adsorbent, *i.e.*, whether it is of the charcoal type, which is incapable of ion formation, or it has the constitution of an ionogen, capable of dissociation into electropositive and electronegative constituents, such, for example, as silicic acid (exhibiting a tendency to dissociate into silicate ion and hydrogen ion) or a metallic hydroxide or some other similarly constituted substance. If an electrolyte such as sodium chloride or methylene blue chloride is brought in contact with charcoal, there is no other possibility but that the positive and negative ions shall be adsorbed in equivalent amounts. This adsorption

can be designated as *equivalent adsorption* of electrolytes. The above prediction was borne out by analyses performed by Rona and the author.[17, 18] The anion and the cation were always adsorbed in equivalent amounts. This equivalence was not exactly obtained, but the error of from 5 to 20 per cent may easily be shown to be due to impurities on the surface of the charcoal. For example, with methylene blue it was found that, in the filtered solution, after complete exhaustion of the methylene blue, some chlorine ion still was present, and this was shown to exist as calcium chloride. The calcium was evidently obtained from the charcoal, and indicates the existence on the surface of a lime salt, possibly a silicate, that has been released according to the principle of reciprocal adsorption. Except for this slight variation, the adsorption of the methylene blue base and the chlorine were equivalent.

It is also conceivable, theoretically, that an hydrolysis accompanies the adsorption, according to the reaction:

Charcoal + methylene blue chloride → Charcoal-methylene blue base + HCl

Although such a reaction has formerly been postulated, there has been no experimental proof of its existence. It has been asserted that when charcoal is placed in a basic dye (the salt of a color base with a mineral acid), and the color removed, an acid solution remains, while, if an acid dye is used, an alkaline solution results. This, however, is not the case. If a salt to be adsorbed is already noticeably hydrolyzed, as perhaps aniline hydrochloride, the case is different. But, for all salts which are not noticeably hydrolyzed, it is possible to state the general fact that hydrolysis is not induced by the process of adsorption. This applies not alone to charcoal but to other absorbents of that type. A few exceptions will be pointed out later.

Although the relatively crude method of chemical analysis seems to show that the adsorption of anions and cations takes place in equivalent amounts, it is still possible that this adsorption deviates from exact equivalence to a degree that is imperceptible by such methods, in that a slightly greater amount of the cation than of the anion may be absorbed, or *vice versa*. This phenomenon apparently causes an electrical potential at the surface, wherein an electrical double layer is formed, the layer adjacent to the charcoal consisting of the more strongly

adsorbed ions, and the layer further removed from the charcoal, of the more weakly adsorbed ions. There would appear an electrical potential difference between the charcoal and the water which could be revealed by cataphoresis of the charcoal particles under the influence of an external electric field or, under other experimental conditions, by electro-endosmose. The charge of the colloid particles may most probably be attributed exclusively to this adsorption potential, and all experiments up to the present have given facts in confirmation of this hypothesis. It can be demonstrated[19, 20] that, in all cases, if a sufficiently adequate experimental method is employed, blood charcoal is positively charged when the cation is most strongly adsorbed, and negatively charged when the anion is most strongly adsorbed.

The following evidence in favor of this theory is deduced from experimental data. From analytical experiments with strong acids and bases it was demonstrated[40] that H^+ and OH^- ions are about equally well adsorbed, and that both of these ions are more readily adsorbed than most other ions. In confirmation of this may be cited experiments on endosmose.[41, 19, 20] Blood charcoal is charged positively by acids and negatively by bases, with an isoelectric point at pH 3.0. Sugar charcoal, on the other hand, does not adsorb the acid anions at all, not even the very easily adsorbed anions of the acid organic dyes. In agreement with this we find that sugar charcoal is never charged positively by acids, but always negatively. This negative charge may, indeed, be diminished by the use of strong acids, but never reversed. On the other hand, among the strong acids there was only a single one found which was not capable of imparting a positive charge to blood charcoal, namely, sulfo-salicylic acid. Now it was found that sulfo-salicylic acid is absorbed by charcoal much more strongly than is any inorganic acid. We are forced to the conclusion that the anion of this acid is more actively adsorbed than the anion of a mineral acid, more actively even than the hydrogen ion. In this case, the portion of the double layer adjacent to the surface of the charcoal must always be negative in the presence of sulfo-salicylic acid. This agrees with the data obtained in experiments on endosmose. The theory postulating the charging of charcoal through inequivalent

ion adsorption seems herewith established. The theory is, however, not applicable to the case of the stability of charcoal suspensions, since these contain a protective colloid, as is the case in india ink. The surface is then not charcoal, but a film of the protective colloid.

The case of an ionic adsorbent is of greater interest from the colloid point of view. We will consider first the case of reciprocal adsorption, as this has been experimentally established and is of general occurrence. The adsorption proceeds as would be anticipated from a purely chemical point of view. For example,

Ca silicate + methylene blue chloride→Methylene blue silicate + $CaCl_2$

whereby the $CaCl_2$ is found in the solution.

Basic ferric chloride (*e.g.*, colloidal ferric hydroxide which contains Cl^- ion) + Na eosine→ferric eosinate + NaCl,

whereby the NaCl is found in the solution. In like manner, in the reaction of a free amorphous acid with an adsorbable salt, as, for example,

Silicic acid + methylene blue chloride→Methylene blue silicate + HCl,

adsorption can only be possible if hydrolysis of the salt spontaneously occurs.

Such reactions, however, have not been realized experimentally up to the present time.[18] For one thing, it is exceedingly difficult to prepare such amorphous bases or acids completely free from their salts. The purest silicic acid that has been prepared always contains calcium, and, when it is colored with methylene blue chloride, it is found to take up only an amount of methylene blue which is equivalent to the calcium which it gives to the solution. The same can be shown equally well with cellulose (filter paper). The purest metallic oxides which adsorb at all always contain anions in combination, as, for example, the common ferric hydroxide always contains chlorine, and when it is colored with eosine the reciprocal exchange of the anions always takes place. If nickel oxide is prepared by heating nickel nitrate, the oxide will adsorb eosine only so long as nitrate or nitrite ions are replaced. If these are completely expelled beforehand, the oxide will not adsorb at all. Nickel oxide was selected because, after heating, it can be rubbed to a fine powder to which we can attribute a large surface sufficient for active adsorption. The objection that the heating may have affected the surface unfavor-

ably cannot entirely be refuted, but it is worthy of mention that a metallic oxide has not yet been prepared which adsorbed an acid dye except by ion exchange, it being presupposed that the dyestuff does not already possess marked colloidal properties.

However, the possibility of hydrolysis as a result of adsorption cannot be generally denied. Neither is it apparent why, under suitable conditions, H^+ ions should not be displaced from the surface by metallic ions. Van Bemmelen[21] long ago described a striking example of this kind. When freshly precipitated and washed manganese dioxide is placed in the solution of a neutral salt, such as sodium chloride or sodium sulfate, the sodium is adsorbed in exchange with hydrogen ions, that is, a small quantity of free mineral acid is formed in the solution. The writer has obtained from such an experiment an HCl solution of pH 4. It has further been shown by Linder and Picton,[22] as also by Whitney and Ober,[23] that, in the precipitation of an arsenic sulfide sol by metallic salts, the metallic cation was exchanged with the H^+ ion, that is, the acid was found free in the filtrate. It may be assumed that the same would result by the coagulation of mastic with neutral salts. In general, therefore, we may not expect hydrolysis by adsorption with a substance as electroneutral as charcoal, but there is no reason to deny the possibility of such a reaction with colloids of a decided acid or basic character. It is, indeed, extraordinary that the anticipated hydrolysis in many cases fails to become manifest. This need not be interpreted as a real absence of a chemical affinity, but as a kind of *passivity*.

An observation in agreement with our point of view is that in each case where a reciprocal adsorption does take place it can be interpreted adequately on the basis of an anticipated chemical exchange. Adsorption occurs when a more difficultly soluble substance will result thereby. Thus, in the special case of manganese dioxide it may be assumed that an insoluble sodium salt of manganous acid is produced, otherwise obtained only through the fusion of the components.

In good agreement with such a chemical conception is the observation of Fajans and Beer[37] and also of Paneth and Horovitz[38] that a radioactive element of a difficultly soluble and heteropolar adsorbent is strongly adsorbed when it forms a difficultly

soluble compound with the same, it being previously ascertained to be present in excess. The chemistry of adsorption is not simple, for the chemical surface of the colloids is not exactly known. Since, for example, according to Freundlich, the surfaces of the particles in a sulfur sol prepared by the method of Odén consist of a polythionic acid, so may we also expect that other simple or even elementary colloids should exhibit a complex condition at their surfaces.

Still another type of adsorption is that known as *electrolytic adsorption*, which does not depend on an exchange, but simply on attraction of the ions of a solid surface which binds them to the surface of the adsorbent. The best known case is that of the silver halides. When a halogen salt, as sodium iodide, is added to a solution of silver nitrate, a precipitate of silver iodide results. Lottermoser[24] pointed out that the electric charge on the precipitated silver iodide is dependent on the quantity ratio of the two salts. If the precipitation is effected with an excess of the halogen salt, the precipitate is electronegative; with an excess of the silver nitrate it is electropositive. The evident explanation is that the surface of the silver halide is covered in the one case with an excess of iodide ion, and in the other case with an excess of silver ion. Lottermoser and Rothe[25] were actually able to demonstrate the adsorption, whether it was produced by the iodide or the silver nitrate. Other properties of the silver iodide also were affected by the nature of the charge. The positive residue is the more sensitive to light; the negative, according to Fajans and Beckerath,[26] easily adsorbs the positive ions of the radioactive isotope of lead, while the positive residue does not. This adsorption capacity of the surface of the silver iodide for one of the two kinds of ions of which it is itself composed is best explained by the theory of Haber.[27, 28] Each silver ion lying on the surface of a crystal of silver iodide (assuming the principle of a cubic space-lattice of silver and iodide ions) has a residual valence for one iodide ion, and each iodide ion lying on the surface has a residual valence for one silver ion. Depending on the quantity ratio of the ions in the solution, either one or the other is adsorbed in excess, and this determines the charge on the surface. In contrast to the reciprocal adsorption (Michaelis and Rona[18] and

Paneth[29]), the above type may be designated as *contact adsorption*, as suggested by Fajans.[30]

Experimental Proof of the Relation between Ion Adsorption and the Coagulation of Colloids

Numerous instances have been brought forward in proof that an electrolyte which produces the coagulation of a colloid is itself adsorbed during the precipitation. In all cases of the following types that have been investigated, this above rule has been found to be the case: when the coagulated ion is adsorbed rather easily by the colloid of opposite charge, when it is a polyvalent ion, when it is a monovalent ion of high adsorbability as the silver ion, or when it is an organic dye or alkaloid ion. In fact, there are only two groups of cases known where an adsorption of the electrolyte has not been demonstrated. The first group embraces cases such as the coagulation of a colloidal acid, for example mastic, by an acid in solution, such as hydrochloric or acetic, the solution becoming in no wise impoverished in acid content. The second case can occur with negative colloids when the coagulating ion is a monovalent and difficultly adsorbed ion, such as sodium.

Cases may first be cited in which the demonstration of adsorption has been readily achieved. The simplest of these, which affords an excellent demonstration of the relation between coagulation and adsorption, is found in those cases where the precipitate contains a colored ion. For example, when mastic is precipitated by a basic dye, such as fuchsin, the coagulum is colored red. Such examples are numerous. Linder and Picton[22] have shown that the cation of the electrolyte used in the coagulation of arsenic sulfide sol is adsorbed, indeed with an exchange of H^+ ion. It was found by Whitney and Ober[23] and by Pauli and Matula[31] that, in the coagulation of ferric hydroxide sol by a sulfate, the sulfate ion is adsorbed in exchange with the chloride ion of the micelles. Michaelis, Rona, and Pincussohn[32] showed that, in the coagulation of a mastic sol, the cation of the coagulating electrolyte is always adsorbed, but such proof could not be obtained with the cations of the monovalent alkali metals, and, furthermore, adsorption could not be demonstrated on coagulation with acids.

The difficulty lay in the fact that with salts so inactive and difficultly adsorbed as sodium chloride the concentrations necessary to bring about coagulation are very much greater than is necessary with active and easily adsorbed ions. Thus, in order to cover the surface of the mastic with a given quantity of ion equivalents, the adsorbed salt, in the case of sodium chloride, must be in equilibrium with a much greater concentration of salt in solution than would be the case with calcium chloride. The relative per cent adsorption of the sodium chloride in a given coagulum will, therefore, be much smaller than in the case of calcium chloride. The actual loss of salts in the solution, even of the easily adsorbed salts, is only a few per cent of the total quantity, so it is to be expected that, with sodium chloride, the loss amounts to only a few tenths of 1 per cent or less. A loss of this order cannot be proved by chemical analysis. There is no compelling reason, however, for assuming any divergence in this case.

The coagulation of colloidal acids by acids in solution is a different matter. With mastic, hydrogen ions are the most active of all of the common ions. Even at a concentration of 10^{-4} N, coagulation proceeds rapidly. It would be expected, therefore, that, if adsorption takes place at all, it would be very easily discovered. But an actual adsorption of an acid cannot be demonstrated. Nor can the competence of the analytical method here be questioned. We are, therefore, forced to the hypothesis that the coagulating action of the acid is not accompanied by an adsorption of the acid. Any comprehensive theory concerning the relation between adsorption and coagulation must account for this special case.

Even in those instances where an electrolyte is added to a sol in amounts too small to effect coagulation, adsorption may usually be demonstrated by ultrafiltration and analysis of the ultrafiltrate, or by a potentiometric ion analysis of the solution. The same quantitative relations as are expressed by the so-called adsorption isotherm of Freundlich may be found by a variation of the quantity of electrolyte added as well as by the usual adsorption experiments. Kohlschütter[42] demonstrated the adsorption of the electrolyte by silver sol, and Lottermoser and Maffia[43, 44] by ferric hydroxide sols. The latter investigators, and also Pauli and Matula,[31]

made use of the principle of potentiometric measurements of ion concentrations in the solutions. The experiments of Lottermoser on adsorption, either of silver ion or of halogen ion, by silver halides have already been discussed in an earlier section.

Theory of the Mutual Relation between Ion Adsorption, Ionic Discharge, and Coagulation

The theory relating ion adsorption and the coagulation of colloids takes for its basis the following postulates:

1. Every electrical charge on the colloid particles favors their stability; discharge favors their coagulation.

2. Adsorption leads to a discharge or, at least, a partial discharge and results, therefore, in a flocculation. We are now concerned with the proof that the coagulation of the colloid is accompanied not only by an adsorption of the electrolyte, which nearly always occurs, but also by the discharge of the particles, which is always effected. This proof is obtainable, in general, by the method of electrical cataphoresis. The velocity of cataphoresis of a particle surrounded by an electrical double layer depends, according to Helmholtz, on the potential of the double layer:

$$V = \frac{\zeta KH}{4\pi\eta}$$

where V is the velocity of cataphoresis, ζ the potential of the double layer, K the dielectric constant of the solvent, 4π a numerical factor, and η the absolute viscosity of the solvent. The factor K was neglected by Helmholtz and was first introduced by Pellat and Perrin,[33] on the assumption that the space between the two shells of the double layer could be regarded as possessing the same dielectric value as the external solvent. The view was formerly suggested in communications by Hardy that coagulation resulted only upon the complete discharge of the double layer. It is not surprising, however, that later investigations showed that complete discharge was not necessary; that a diminishing of the charge to a certain low value was sufficient to effect the coagulation. This begins always, for any given sol, when, no matter how this value is achieved, the potential has fallen to a definite

absolute value. This was first pointed out by Ellis[34] and Powis[35] for oil emulsions. It was immaterial whether the discharge was effected by $ThCl_4$, $AlCl_3$, $BaCl_2$, or KCl. The coagulation of the emulsion began in each case when the potential had decreased to 30 to 40 millivolts (Th 40, Al 30, Ba 28, K 30 millivolts). This represents, therefore, the *critical potential.* It will be observed that the agreement of the critical potentials for different cations is not perfect, and even greater differences were observed in the coagulation of arsenic sulfide sol, investigated by Powis. These were as follows: $Th(NO_3)_4$ 26, $AlCl_3$ 25, $BaCl_2$ 26, but KCl 44 and HCl 30 millivolts. Even here, however, the values are of the same order, and the conclusion is reached that the magnitude of the potential of the double layer is, indeed, the most important, if not the only decisive, factor in the coagulation.

Both concepts referred to at the beginning of the chapter remain correct as stated, but now require a more detailed discussion.

Although the content of both of these postulates is today entirely familiar to colloid chemists, their inner significance is very often not clearly understood. The relation is frequently stated in the following manner: When a negative particle adsorbs positive ions it must be discharged, and, therefore, coagulating action is associated only with ions of opposite charge and the ability to adsorb is proportional to the magnitude of the difference in charge. This description appears at first sight to be very simple, but it is, when so expressed, not strictly representative of the state of affairs. It implies the somewhat naïve concept that the colloid particles are charged in a manner similar to that of a stick of sealing wax which has been rubbed, and that the discharge through adsorption of an oppositely charged ion is analogous to discharge of the negative stick of sealing wax by covering with a positively charged plate of tin foil. The difference, however, lies in the fact that the colloid particles are not charged in the same manner as the sealing wax, but rather by virtue of being surrounded with an electric double layer. The analogy would be to a stick of sealing wax closely surrounded by the cloth, through the rubbing of which the electricity is produced. As soon, however, as we remove the cloth we disrupt the "double layer." The electricity becomes "free" and we have then no analogy with colloids. It is further assumed that

colloid particles of like charge cause an electric repulsion and so lessen the probability of collision of the colloid particles. But when we have a perfect double layer, this repulsion is not understandable on the basis of Coulomb's law without further amplification. It we imagine the colloid particles as consisting of spheres, we can picture the outer energy effects of the electricity of the surface-charged particles as if the total charge were concentrated at the center of the sphere. Since the inner and outer shells of the double layer have the same charge of opposite sign and have a common middle point, they immediately neutralize each other, and an energy component extended outwards is not explained. The solution of this paradox lies in the following. We may regard the charge on the surface of a sphere as concentrated at its center only when the magnitude of the charge is the same over the entire surface, and this will be the case with a given colloid particle. But if two such particles approach very close to each other, a change in the distribution of the charge will take place, due to the electrostatic action. The moving outer double layers becomes orientated, because of the electrostatic repulsion, so that the double layer is thinner on the sides turned towards each other and denser on the sides turned away from each other. We may, therefore, no longer regard the charge as concentrated in the center of the sphere but rather in the center of an electrostatic field, which is not coincident with the geometric center. This idea may be developed further and leads to the conclusion that the spheres repel each other, but not by the simple postulate of Coulomb's law, inversely proportional to the square of the distance, the repulsion decreasing much more rapidly with increase of distance. The repulsion is, therefore, imperceptible when the particles are far apart, and becomes apparent only when the particles approach very close to each other. Nor does the double layer itself act to prevent contact by exerting a repulsive action from a distance. Indeed, the behavior may be likened to that of an elastic cushion, which at first offers no opposition to approach, but at the moment of contact exerts a repulsive power.

The relation of adsorption to ionic discharge now remains to be discussed. The mechanism of the discharge through ion adsorption is divided for consideration into contact adsorption and reciprocal adsorption.

With contact adsorption the case is a simple one. Let us return to the example of silver iodide. Fajans and Frankenburger[30] have again called attention to a phenomenon that may easily be carried out by any analyst. If a titration is undertaken wherein $AgNO_3$ is added gradually to a solution of NaI, there is first formed a cloudiness of the AgI, which has little tendency to settle, and a colloidal solution results. As we approach the end point the precipitate rapidly coagulates and separates. If we pass beyond the end point, however, by rapid overtitration, the precipitate remains as before with no decided tendency to coagulate. The conditions for flocculation are dependent on the discharge. Before the end point is reached the particles are negative through adsorption of iodide ions, but upon overtitration the particles are positive through adsorption of silver ions. Here there is no difficulty in the interpretation.

With reciprocal adsorption the case is not so simple. In this type we may think of the charge as arising in the following manner: The substance of each colloid particle exerts a tendency to dissociate into ions, one of these being of the usual type and the other, being incapable of diffusion, remaining associated as a micelle. Thus a double layer results, and the laws of the electrical condenser may be applied, with slight modification, as has been done by Helmholtz.

Accordingly, in the double layer, we may differentiate the following factors:

1. The electrical surface density σ of each layer.

2. The distance between the two layers or the thickness D of the double layer.

3. The potential difference p of the layers, or, to be more exact, the difference in the potential which the total charge of the condenser exerts upon a point of one layer and that which it exerts upon a point in the other layer. To relate these factors:

$$p = \frac{4\pi\sigma D}{K}$$

where K is the dielectric constant of the medium between the layers. But Gouy[45] has pointed out that at least the outer shell of the double layer, which consists of the free-moving ions, cannot

be conceived as a surface layer, but possesses a certain depth or field of diffusion, in that the concentration of the ions constituting the outer shell gradually becomes identical with the concentration of the same kind of ions in the solution.

We may not, therefore, speak of a definite thickness of the double layer, but may picture the action only as similar to that of a surface condenser, in which the thickness is equal to that of a certain average thickness of the double layer of the diffuse condenser. This thickness is, indeed, only a calculated value, and, if we wish to make use of it, we may simplify the theory in the following manner. Since the surface of a given colloid particle has a definite number of molecules capable of dissociating, the density of the charge on a given colloid will not, in general, be variable. All diffusible ions will remain at a definite distance from the colloid ion, depending on the nature of the diffusible ion. In determining the potential of such a condenser, only the average thickness of the double layer need be considered. The dielectric constant also should be considered, for we cannot assume that the medium between two nearly adjacent ions is the same as that between two distant ions, which is simply the solvent. In all cases we may conceive the condenser to be changed only by varying the average thickness, if we wish to keep clear the concept of a fixed potential. The value of the concept lies in this, that upon the magnitude of this potential depends the mutual repulsion of the micelles. If all the ions of the outer shell are placed infinitely near to the oppositely charged ions of the inner shell, the potential of the condenser is zero, and two such condensers taken as a whole exert no influence upon each other.

By combining this view with the experience that, in general, the coagulating ions undergo reciprocal adsorption with others, we arrive at the following generalization. The adsorption of an ion signifies the replacement of an ion, present originally in the outer shell of the double layer, by another of like charge. This exchange takes place when the new ion is able to approach closer to the inner shell of the double layer and hence to diminish the potential difference between the two layers and hence to diminish the repulsion of the micelles. Adsorption takes place when, by its accomplishment, the potential electrial energy of

the colloid particles will be diminished, or when electrical work may be done by the adsorption.

We are not able to say, in general, what property, according to this view, an ion must have in order to displace another ion from the outer shell of the double layer. But several general observations are at once clear. A bivalent ion always tends to displace a univalent ion, as the former can always approach closer to the inner shell of the double layer than the latter. The electrical attraction of the inner shell upon two univalent ions and upon one bivalent ion is the same, but, other conditions being the same, the diffusion pressure opposing this attraction is twice as great for two univalent ions as for one divalent ion. Still other constitutional influences may play a part which cannot here be surveyed individually. The strongest influence is that of valence, as can be easily understood.

It still remains for us to bring into harmony with this concept the fact that, for example, mastic is coagulated by acid without the latter being adsorbed. The outer shell of the double layer consists, no doubt in the case of mastic, of H^+ ions only, when the colloid is in pure water. These H^+ ions are dissociated from the mastic, not adsorbed from the water. The average thickness of the double layer is determined, on the one hand, by the electrostatic attraction of both layers for each other; on the other hand, by the diffusion gradient of the H^+ ion from the outer shell of the double layer to the rest of the solution. This gradient depends on the concentration of the H^+ ion in the solution. An increase in concentration causes a decrease in the average thickness of the double layer and leads to a decrease in potential, and, therefore, also to coagulation even without adsorption.

The foregoing may be summarized in the following proposition. A colloid is discharged and coagulated by an electrolyte when, either through the exchange of one kind of ion by another kind of ion or through opposed osmotic action of the same kind of ion which forms the outer shell of the double layer, the *potential electrical energy of the system* can be diminished. A quantitative formulation of this principle appears, however, as yet premature, since too many necessary data are missing.

REFERENCES

1. Gibbs, J. Willard: *Trans. Connecticut Academy*, **2** and **3** (1875–1878).
2. Thomson, J. J.: "Applications of Thermodynamics to Physics and Chemistry."
3. Michaelis: "Die Wasserstoffionenconcentration," 2nd ed., Berlin, 1922, p. 200.
4. Freundlich: "Capillarchemie," 2nd ed., Leipzig, 1922.
5. Michaelis and Rona: *Biochem. Z.*, **102** (1920), 268.
6. Bayliss: *Proc. Roy. Soc.* (London), **84** (1914), 586.
7. Haller: *Kolloid-Z.*, **22** (1918), 113; **24** (1919), 56; **27** (1920), 30.
8. Willstaetter: *Ber.*, **37** (1904), 3758.
9. Gans: *Jahrb. kgl. Preuss. Geolog.*, **26** (1905), 179; **27** (1906), 63.
10. Schulze: *Z. physik. Chem.*, **89** (1915), 168.
11. Freundlich: *Ibid.*, **44** (1903), 136.
12. Ostwald, Wo.: *Kolloidchem. Beihefte*, **10** (1919), 204.
13. Zsigmondy: *Z. Electrochem.*, **22** (1916), 102; *Z. anorg. allgem. Chem.*, **96** (1916), 265.
14. Freundlich and Rona: *Biochem. Z.*, **81** (1917), 87.
15. Rona and Györgyi: *Ibid.*, **105** (1920), 133.
16. Kruyt and van Duin: *Kolloidchem. Beihefte*, **5** (1914), 269.
17. Rona and Michaelis: *Biochem. Z.*, **94** (1919), 240.
18. Michaelis and Rona: *Ibid.*, **97** (1919), 57.
19. Michaelis: *Z. Electrochem.*, **28** (1922), 453.
20. Umetsu: *Biochem. Z.*, **135** (1923), 442.
21. Van Bemmelen: *J. prakt. Chem.*, **23** (1881), 342; "Die Adsorption," Dresden, 1910.
22. Linder and Picton: *J. Chem. Soc.*, **87** (1905), 1908.
23. Whitney and Ober: *Z. physik. Chem.*, **39** (1902), 630.
24. Lottermoser: *J. prakt. Chem.*, **72** (1905), 39; **73** (1906), 374; *Z. physik. Chem.*, **60** (1907), 451.
25. Lottermoser and Rothe: *Z. physik. Chem.*, **62** (1908), 359.
26. Fajans and Beckerath: *Ibid.*, **97** (1921), 478.
27. Haber: *J. Soc. Chem. Ind.*, **33** (1914), 50; *Z. Electrochem.*, **20** (1914), 521.
28. Langmuir: *Chem. Met. Eng.*, **15** (1916), 469; *Phys. Rev.*, **6** (1915), 79; **8** (1916), 149; *J. Am. Chem. Soc.*, **38** (1916), 2221; **39** (1917), 1848; **40** (1918), 1361.
29. Paneth: *Z. physik. Chem.*, **101** (1922), 445.
30. Fajans and Frankenburger: *Ibid.*, **105** (1923), 255.
31. Pauli and Matula: *Kolloid-Z.*, **21** (1917), 49.
32. Michaelis, Pincussohn, and Rona: *Biochem. Z.*, **6** (1907), 1.
33. Perrin: *Chim. Phys.*, **2** (1904), 601; **3** (1905), 50.
34. Ellis: *Z. physik. Chem.*, **80** (1912), 597.
35. Powis: *Ibid.*, **89** (1915), 186.
36. Hardy: *Proc. Roy. Soc.* (London), **66** (1900), 110.

37. Fajans and Beer: *Ber.*, **46** (1913), 3486; Fajans and Richter: *Ibid.*, **48** (1914), 700.
38. Paneth: *Physik. Z.*, **15** (1914), 924; Paneth and Horovitz: *Z. physik. Chem.*, **89** (1915), 513; *Wiener Akademie Wissensch.*, **123** (1915), 1819.
39. Lachs and Michaelis: *Kolloid-Z.*, **9** (1911), 275; **31** (1922), 203.
40. Rona and Michaelis: *Biochem. Z.*, **97** (1919), 85.
41. Gyemant: *Kolloid-Z.*, **28** (1921), 103.
42. Kohlschütter: *Z. Electrochem.*, **14** (1908), 49.
43. Lottermoser and Maffia: *Ber.*, **43** (1910), 3613.
44. Maffia: *Kolloidchem. Beihefte*, **3** (1911), 85.
45. Gouy: *J. Phys.*, (4), **9** (1910), 457; *Compt. rend.*, **149** (1909), 654; *Ann. Phys.*, (9), **7** (1917), 129.

CHAPTER X

ADSORPTION AND CATALYSIS

By

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The increased concentration of reacting substances at the surface of an adsorbing catalyst will in itself mean an increased reaction velocity; but this factor seems relatively small in most cases of contact catalysis, except, perhaps, in some experiments with silica where we seem to be dealing primarily with a condensation in the pores rather than with adsorption. A pressure of 2,000 atmospheres is not sufficient to make hydrogen and oxygen react with measurable velocity at ordinary temperatures.[1] It is not easy to see how differences in concentration can account for alcohol decomposing chiefly to ethylene and water in one case, and chiefly to acetaldehyde and hydrogen in another.

What actually happens is that the reacting substances are activated as a result of adsorption; but we do not yet know just what we mean by activation. When two saturated compounds react, the first stage must be a dissociation, which involves the breaking of a regular bond, or it must be an addition, which involves the opening of a secondary valence[2] or contravalence. One of the problems of contact catalysis is to determine in any particular case which bond has been broken, opened, or activated, the three terms being synonymous. In aqueous solutions many substances are activated by dissociation into ions.

Langmuir[3] considers that adsorption involves the temporary union of the adsorbed substance with the adsorbing material; but he leaves it undecided for the present just where and how the

[1] See also BURDICK: *J. Am. Chem. Soc.*, **44** (1922), 240.

[2] For a discussion of primary and secondary adsorption, see BENTON: *J. Am. Chem. Soc.*, **45** (1923), 887.

[3] *J. Am. Chem. Soc.*, **37** (1915), 1139; **38** (1916), 1145, 2221; **39** (1917), 1848.

union takes place, except in a very general way. If a substance is adsorbed from aqueous solution by charcoal, for instance, the more polar portion of the molecule is assumed to project into the water, producing what is known as "oriented" adsorption. There are, then, two possible ways in which reaction may take place. The adsorbed or captive molecule may be bombarded effectively by free molecules, causing a reaction. On this assumption the reaction will probably take place at the free end of the captive molecule. As the bond between the adsorbed substance and the adsorbing agent makes or breaks during dynamic equilibrium, we have, temporarily, an activated radical and this may react with another activated radical or with a neutral molecule. On this assumption, the reaction will take place chiefly at what is temporarily the captive end of the molecule at a moment when the molecule itself is free. We do not yet know whether it is chiefly the captive molecule or the free radical which reacts, or whether both may be considered as activated. Kruyt and van Duin[4] believe that it is the free end of the captive molecule which reacts.

If the reaction takes place at a non-polar, or less polar, portion of the molecule, this part is turned away from the aqueous phase and from the substances dissolved in it. If the two reacting substances are more or less polar, it may be that they will be adsorbed in such a way that the reacting portions are turned away from each other. From this point of view, it is clear why we obtained a negative catalysis at first in spite of the adsorption.

On the other hand, the experiments of D. Berthelot and Gaudechon[5] indicate that ultra-violet light of suitable wavelengths will bring about all the reactions which can be produced by catalytic agents; and one has no captive molecules when dealing with ultra-violet light. It, therefore, seems probable that, in most cases, the active masses are the free radicals at the moment before or after the molecules are combined with the adsorbing material. When substances are activated photochemically, there is no question whether a definite or an indefinite intermediate product is formed with the catalytic agent, because light is not a ponderable substance.

[4] *Rec. trav. chim. Pays-Bas.* (4), **2** (1921), 249.

[5] *Compt. rend.*, **150** (1910), 1169, 1327, 1517, 1690; **151**, 395, 478, 1349; **152** (1911), 262, 376, 522; **153**, 383.

While Langmuir considers that an adsorbed substance is united chemically with the adsorbing material, he does not mean by this, as many people have assumed, that a chemical compound of the ordinary type is formed, one described by the law of definite and multiple proportions. Langmuir looks upon a coherent mass of charcoal as a giant molecule, and when chlorine is adsorbed by charcoal, he does not postulate the formation of carbon tetrachloride, tetrachloroethylene, hexachloroethane, hexachlorobenzene, or anything of that sort. He means that the whole of the carbon and the whole of the chlorine are to be considered as forming a compound, the composition of this so-called compound varying continuously as the chlorine is pumped out. If one wants to call such a system a chemical compound, it should be called an indefinite compound to differentiate it from the definite compounds as known to Dalton.

There is, of course, no theoretical reason why contact catalysis should not involve the intermediate formation of definite chemical compounds, and this is apparently the case when a hydrogen peroxide solution reacts with mercury,[6] when acetic acid is passed over heated barium carbonate,[7] or when carbon monoxide is oxidized in presence of mixed oxides[8] of cobalt, manganese, etc.; but it is important to know whether definite intermediate compounds are formed or not. If we are dealing with adsorption, no definite intermediate compound is formed. It is very probable that some cases now assumed to involve definite intermediate compounds may prove really to be activation by adsorption. In the catalytic oxidation of carbon monoxide, it is assumed that there is alternate (or simultaneous) reduction and oxidation of the catalyst. The oxidation carrier is supposed to oxidize the carbon monoxide and to be reoxidized itself by the oxygen of the air. Unfortunately, the rate of oxidation of carbon monoxide by the higher oxides is relatively slow, so that the alternation from one stage of oxidation of the catalyst to another may be a negligible factor in the reaction velocity. Bray believes that it is useless to try to decide whether, at the dynamic equilibrium,

[6] Bredig and von Antropoff: *Z. Elektrochem.*, **12** (1906), 581; von Antropoff: *J. prakt. Chem.* (2), **77** (1908), 273.

[7] Squibb: *J. Am. Chem. Soc.*, **17** (1895), 187.

[8] Lamb, Bray and Frazer: *J. Ind. Eng. Chem.*, **12** (1920), 217.

a molecule of oxygen at the surface of the catalyst actually changes some of a lower oxide to a higher (and the reverse change with carbon monoxide[9]) or whether the oxygen is merely held on the surface in an active condition ready to combine with carbon monoxide. In either case, all the processes are taking place simultaneously.

The oxidation of alcohol by air in the presence of osmium tetroxide can easily be run in two stages,[10] because osmium tetroxide will oxidize alcohol in the absence of air, and air will oxidize the dioxide back to the tetroxide; but we do not know whether the single reaction velocities are sufficient to account for the rate of catalysis. If not, we shall have to postulate activation of oxygen independently of the definite chemical reaction.

It is a simple matter to account for the decomposition of alcohol into acetaldehyde and hydrogen by nickel, and into ethylene and water in presence of alumina on the basis of differently oriented adsorption. Adkins[11] has shown, however, that differently prepared samples of alumina decompose ethyl acetate in different ways. He believes that there is some connection between the size of the molecular pores of the alumina and the molecular diameters of the decomposition products, while Taylor considers that it is a case of selective adsorption on the alumina, the ethyl acetate being adsorbed on or by the aluminum atoms in one case and on the oxygen atoms in the other case. For the moment these are both unproved guesses.

Pease and Taylor[12] have found that the reduction of copper oxide by hydrogen takes place practically only at the interface between copper and cuprous oxide. Years ago, Campbell[13] recommended the use of palladinized copper oxide in combustions. Any advantage of such an arrangement must have been due to action at an interface. Lewis[14] found that finely divided plati-

[9] Benton considers that he has proved this. *J. Am. Chem. Soc.*, **45** (1923), 900.

[10] Hofmann: *Ber.* **45** (1912), 3329; **46** (1913), 1657, 2854; **48** (1915), 1585.

[11] *J. Am. Chem. Soc.*, **44** (1922), 385, 2175.

[12] *J. Am. Chem. Soc.*, **43** (1921), 2179; Langmuir: *Trans. Faraday Soc.*, **17** (1922), 607.

[13] *J. Am. Chem. Soc.*, **17** (1895), 681.

[14] *Z. physik. Chem.*, **52** (1905), 310; **55** (1906), 449; *J. Am. Chem. Soc.*, **28** (1906), 139.

num, silver, and manganese dioxide catalyze the dissociation of silver oxide into silver and oxygen. This is probably also a reaction at the interface and the same explanation probably holds for the action of finely divided platinum and certain metallic oxides[15] upon the dissociation of mercuric oxide.

A striking case of action at an interface, and one which has been known for a long time, is the zinc-copper couple of Gladstone and Tribe.[16] With copper precipitated on, and in intimate contact with, zinc, it is possible to decompose many of the alkyl halides at moderate temperatures. When the couple is made from zinc dust,[17] the preparation of zinc methyl can easily be shown as a lecture experiment. The couple decomposes bromoform, giving methane and acetylene.[18] Thorpe[19] used the couple as a means of reducing nitrates, iodates, and chlorates quantitatively, and, under his direction, Eccles[20] used it to determine chlorates in the presence of perchlorates, the former being reduced to chlorides and the latter not. Devarda's alloy[21] seems to be another form of the same thing. It is not customary to consider the action of the zinc-copper couple as catalytic, because the zinc reacts; but it is catalytic as regards the copper. In aqueous solutions the action of the couple is undoubtedly electrolytic and it may perhaps always be so. With the organic substances the infinitesimal distance between the two metals may counterbalance the high resistance of the organic liquid. When copper oxide is reduced by hydrogen, we do not know whether this is a limiting case of electrolysis or whether there is a special activation owing to the hydrogen being adsorbed simultaneously by the two substances at the interface.

[15] Taylor and Hulett: *J. Phys. Chem.*, **17** (1913), 565; *J. Am. Chem. Soc.*, **44** (1922), 1443; Kendall and Fuchs: **43** (1921), 2017; **44** (1922), 1447.

[16] *Proc. Roy. Soc.*, **20** (1872), 218; *J. Chem. Soc.*, **25** (1872), 461; **26** (1873), 445, 453, 678, 961; **27** (1874), 208, 406, 410, 615; **28** (1875), 208; **30** (1876), 37; **31** (1877), 561; **33** (1878), 139, 306; **35** (1879), 107, 172, 567.

[17] Lachmann: *Am. Chem. J.*, **19** (1897), 410.

[18] *Cf.* Sargent: *J. Phys. Chem.*, **16** (1912), 407.

[19] *J. Chem. Soc.*, **26** (1873), 541.

[20] *Ibid.*, **29** (1876), 856.

[21] *Z. anal. Chem.*, **33** (1894), 113; Allen: *J. Ind. Eng. Chem.*, **7** (1915), 522.

Another phenomenon which may be due to an action at an interface is that known as *promoter action.*[22] Reduced iron is the most effective single catalyst that can be used commercially in the ammonia synthesis, but its activity can be increased by the addition of small amounts of molybdenum, tungsten, or cerium. If these substances form separate phases, they will give rise to interfaces; but, if they form solid solutions, the question of action at an interface does not arise. While the action of these promoters, as they are called, may be at the interface, this is probably not the important factor, because the maximum effect comes at low concentrations, long before the interface is a maximum. While the theory of promoter action has not been worked out, a plausible guess is that the catalytic agent activates one reacting substance chiefly, and that the promoter activates the other. Thus, in the ammonia synthesis, it may be that iron activates hydrogen chiefly, so that we have hydrogenation of the nitrogen. The molybdenum may tend to activate the nitrogen or may increase the activation of the nitrogen, thus causing nitridation of the hydrogen. Such a state of things is not impossible, theoretically. When a dye reacts with the oxygen of the air under the influence of light, the light may make the oxygen so active that it will oxidize the dye, or the light may make the dye active, in which case the activated dye will reduce the oxygen. Whether it is primarily the dye or the oxygen that is activated depends on whether the effective light corresponds to an absorption band for the dye or for the oxygen. Experimentally, it appears that, under ordinary conditions, it is apt to be the dye which is activated.[23]

Promoter action is by no means confined to the ammonia synthesis. Pease and Taylor[24] have collected the data on promoter action and it appears that the phenomenon is a fairly common one. Ipatiew[25] found that copper oxide in an iron tube is much more effective in causing the hydrogenation of amylene than is copper oxide in a copper tube. The Badische Company[26]

[22] Rideal and Taylor: "Catalysis in Theory and Practice," 1919, p. 31.
[23] Bredig and Pemsel: *Archiv wiss. Photographie*, **1** (1899), 33.
[24] *J. Phys. Chem.*, **24** (1920), 241.
[25] *Ber.* **43** (1910), 3387.
[26] D. R. P. 282, 782 (1913).

states that hydrogenation of fats is accelerated by the presence of tellurium. Dewar and Liebmann[27] claim that a mixture of nickel and copper oxides can be reduced in cottonseed oil at 190°C. and will hydrogenate the oil rapidly at that temperature, whereas nickel oxide alone requires a temperature of about 250° for the reduction. Hochstetter[28] found that a mixture of silver and copper is more effective for the synthesis of formaldehyde from methanol than either metal singly. Maxted[29] states that bismuth, tungsten, and copper make iron active in the ammonia oxidation. Mention has been made of the fact that mixed oxides are more efficient in oxidizing carbon monoxide than any of the oxides alone. This may be a factor in the behavior of the Welsbach mantle, though it has not been proved.

While there is no activation and, consequently, no contact catalysis unless we have adsorption, the converse is not true that the catalytic action is greater the greater the adsorption. With any given catalyst and any given reaction, the maximum catalytic activity does not necessarily coincide with the maximum adsorption, and usually does not do so, in fact. Adsorption is always greatest at low temperatures, whereas there is often very little catalytic action below a certain ill-defined temperature. There are three possible causes for this. The adsorption of some one of the reacting substances or of the reaction products may be so great as to interfere with the free flow of matter to and from the surface of the catalyst, or it may be that the activation is greater at higher temperatures or—which is certainly a factor—that the rate of reaction of the activated gases is very much greater at higher temperatures. We should, then, have adsorption decreasing with rising temperature, activation varying in an unknown way with the temperature, and the rate of reaction of the activated gases increasing rapidly with rise of temperature.

Taylor and Burns[30] consider that:

> Reaction is the resultant of at least two factors, the adsorption factor and the temperature factor. There is evidence as to how these two factors operate. For example, it is known that ethylene and hydrogen

[27] U. S. P. 1268692, 1275405.
[28] U. S. P. 1100076, 1110289.
[29] *J. Soc. Chem. Ind.*, **36** (1917), 777.
[30] *J. Am. Chem. Soc.*, **43** (1921), 1283.

can be caused to react by purely thermal means. The temperatures required are high, being in the region of 500°. With a nickel catalyst present, reaction occurs from room temperature upward, and strong adsorption of both gases is shown by nickel. With copper, a temperature of 150° is required for incipient action and adsorption by this metal is much less pronounced than in the case of nickel. Similar observations hold in respect to the conversion of carbon monoxide and hydrogen by means of nickel and cobalt, the temperature required in the use of cobalt, the less efficient adsorption agent, being some 90° higher than with nickel for similar rates of reaction. It will, therefore, appear that the adsorption capacity is an index of the temperature at which reaction can be induced. Where adsorption is strong we have, presumably, a more marked or more frequent displacement of the stable configuration of the molecule than with a weak adsorption. Consequently, a lower temperature will effect interaction.

On another page Taylor and Burns say that:

The measurements with active nickel catalysts and with inactive nickel obtained by reduction of the oxide at elevated temperatures form, we believe, convincing experimental demonstration that the destruction of catalytic activity is accompanied by an almost complete suppression of adsorption power.

Benton[31] concludes that:

No connection whatever exists between the extent of secondary adsorption and catalytic activity for carbon monoxide oxidation. The primary adsorption of carbon monoxide, however, is in exactly the same order as the catalytic activity.

It seems to be certain that adsorption depends essentially on a porous structure. H. Briggs[32] considers that a smooth or vitreous surface has a relatively low catalytic action. Taylor and Burns state that 97 per cent of the adsorptive capacity of nickel for several gases is destroyed by heating the nickel to 600°. Though some sintering does take place, there is no reason to suppose that the new surface is only 3 per cent of the old one. There has been a change in the nature of the surface. Armstrong and Hilditch[33] have obtained similar, though less striking, results with nickel, while Gilfillan[34] has shown that, by calcining

[31] *J. Am. Chem. Soc.*, **45** (1923), 901.
[32] *Proc. Roy. Soc.*, **100** A (1921), 97.
[33] *Proc. Roy. Soc.*, **99** A (1921), 490.
[34] *J. Am. Chem. Soc.*, **44** (1922), 1323.

thoria strongly or by heating it for a long time at a lower temperature, the oxide can be made practically inert so far as the dehydration of alcohol is concerned. Kramer and Reid[35] have made a very inert thoria in an unexpected way by dropping thorium nitrate into a red hot crucible. The rapid decomposition gives a very bulky thoria, 35 g. of it occupying a liter. In spite of the enormous surface, this thoria was practically inactive as a catalyst, presumably because the surface was vitrified and not porous.

Palmer[36] could not precipitate copper electrolytically so that it would dehydrogenate ethyl or isopropyl alcohol at any temperature between 200 and 300°. He considers that there are two kinds of copper, that obtained by electrolysis being composed of cupric copper atoms, while that from copper oxide is a mixture of cupric copper atoms and cuprous copper atoms. The two hypothetical types of copper are assumed to be heterotopic, to have different surface lattices, to possess different chemical properties,[37] and to adsorb differently. Palmer assumes, further, that the ratio of the two types of copper will vary with the reducing agent and with the temperature at which reduction takes place. Unfortunately for this flexible hypothesis, samples of copper prepared by Benton at Princeton by reduction of different samples of copper oxide at different temperatures all showed the characteristic copper metal lattice when examined by the x-ray method at the Research Laboratory of the General Electric Company at Schenectady. It is, therefore, not necessary to discuss whether electrolytic copper is cupric copper. The whole difficulty is undoubtedly that Palmer did not precipitate his copper in a sufficiently porous form.

While the catalytic activity can be reduced practically to zero by a change in the structure of the catalytic agent, the same result can also be obtained by the action of *poisons*, as they are called. In technical catalytic processes, the great difficulty is to keep the catalyst active, as the presence of any one of a number of substances even in minute amount will *poison* the catalytic agent and render it inert. Up to a few years ago, this poisoning

[35] *J. Am. Chem. Soc.*, **43** (1921), 882.
[36] *Proc. Roy. Soc.*, **98 A** (1920), 15; **99 A** (1921), 412.
[37] Soddy: *J. Chem. Soc.*, **115** (1919,) 23.

of the catalytic agent was considered a most mysterious phenomenon, but the theory of it is now quite satisfactory. Since the reaction takes place in or at the surface of the catalytic agent, any substance, gas, liquid, or solid which decreases the rate at which the reacting substances reach the catalytic surface,[38] or which prevents them from reaching it,[39] will decrease the reaction velocity and may destroy the catalytic action completely.

Berliner[40] has shown that traces of fatty vapors from the air or from the grease on the stop-cocks will decrease the adsorption of hydrogen by palladium from about 900 volumes to nothing. Pollard[41] observed a similar decrease with platinized asbestos, from about 160 volumes to a negligible amount. Faraday[42] proved that traces of grease destroy the catalytic action of platinum black. Lunge and Harbeck[43] found that carbon monoxide inhibits practically completely the catalytic action of platinum on a mixture of ethylene and hydrogen. Taylor and Burns[44] have shown that this is because carbon monoxide decreases the adsorption of hydrogen by platinum black. Working under more favorable conditions, Pollard[45] has obtained a similar, but more striking, result. With platinized asbestos, kept very clean from grease, he obtained an adsorption of 160 volumes of hydrogen per volume of platinum. On introducing carbon monoxide the hydrogen adsorption dropped to about 7 volumes, which was practically negligible under the conditions of the experiment. Taylor and Burns conclude from their experiments that, even when the pressure of carbon monoxide does not exceed a few centimeters, the platinum surface is probably covered so thoroughly with carbon monoxide that hydrogen and ethylene are unable to reach it. They also point out that platinum, which holds carbon monoxide so tenaciously, is not a good catalytic agent for the reduction of carbon monoxide to methane, whereas this reduction takes place readily at a palladium surface, from

[38] Taylor: *Trans. Am. Electrochem. Soc.*, **36** (1919), 149.
[39] Bancroft: *J. Phys. Chem.*, **21** (1917), 734.
[40] *Wied. Ann.*, **35** (1888), 903.
[41] *J. Phys. Chem.*, **27** (1923), 356.
[42] "Experimental Researches on Electricity," **1** (1839), 185.
[43] *Z. anorg. Chem.*, **16** (1896), 50.
[44] *J. Am. Chem. Soc.*, **42** (1921), 1285.
[45] *J. Phys. Chem.*, **27** (1923), 356.

which carbon monoxide can be displaced easily by hydrogen at ordinary temperatures.

Schönbein[46] pointed out that the hydrides of sulfur, tellurium, selenium, phosphorus, arsenic, and antimony act very energetically in cutting down the action of platinum on mixtures of air with hydrogen or ether. Since he did not realize that an adsorbed gas film might keep out other gases, he decided that these hydrides must decompose and plate out a solid film on the platinum. This hypothesis is not necessary to account for the phenomenon; but Schönbein was right in at least one case. The most complete experimental study of poisons made so far is by Maxted,[47] who has shown that hydrogen sulfide is decomposed by platinum black with the evolution of hydrogen, and that the "sulfurized" platinum does not adsorb hydrogen. With varying amounts of hydrogen sulfide, both the adsorbing power and the catalytic action decrease linearly over a certain range of concentrations. When platinum is poisoned by lead, 1 mg. of lead poisons nearly 9 mg. of platinum, this figure applying only to platinum black prepared in a given way and, therefore, having a given ratio of active surface to mass.

Maxted has also made experiments with mercuric chloride, mercuric nitrate, and lead acetate on platinum prepared by Loew's method, the catalysis of hydrogen peroxide being taken as the test of the poisoning. With mercuric chloride it made little or no difference whether the platinum was left in contact with the mercuric chloride solution for 30 minutes or for 12 hours. This shows that there is no progressive deterioration of the platinum and that the change takes place fairly promptly. The curve obtained by plotting the catalytic activity of the platinum against the poison content is practically linear until at least 70 per cent of the original activity has been suppressed.

Twenty-five years ago, Bredig[48] showed that many substances poison the action of platinum on hydrogen peroxide solutions. The rate of decomposition of hydrogen peroxide by a given

[46] *J. prakt. Chem.*, **29** (1843), 238.

[47] *J. Chem. Soc.*, **115** (1919), 1050; **117** (1920), 501; **119** (1921), 225, 1286; **121** (1922), 1760.

[48] Bredig and von Berneck: *Z. physik. Chem.*, **31** (1899), 258; Bredig and Ikeda: **37** (1901), 1.

suspension of colloidal platinum is reduced approximately to one-half by M/20,000,000 HCN, M/2,000,000 $HgCl_2$, and M/300,000 H_2S. Since Schönbein[49] had shown that these substances decrease the catalytic action of the red blood corpuscles on a solution of hydrogen peroxide, and since the catalytic agent is the organic ferment, hæmase, in the blood corpuscles, Bredig called his colloidal metals inorganic ferments.

It seems probable that the poisons are adsorbed strongly by the colloidal platinum and, therefore, prevent the adsorption and decomposition of hydrogen peroxide;[50] but the only data on the subject are those obtained recently by Maxted.

Pease[51] has shown that the vapor from 1 cu. mm. of liquid mercury introduced into 100 g. of a reduced copper catalyst inhibits completely the reaction between hydrogen and ethylene at 0°. Furthermore, the reaction is still extremely slow at 100°. The mercury suppresses practically completely the adsorption of hydrogen by the copper, but has very little effect on the adsorption of ethylene.

Ueno[52] has studied the effect of various additions to the nickel catalyst in the hydrogenation of oils. There is nothing in the abstract to show whether any theoretical conclusions were drawn, so presumably that was not the case.

All of the six alkali metals act as negative catalyzers; magnesium, strontium, calcium, and beryllium retard it; aluminum and cerium are negative catalyzers; a large amount of iron also retards it. Manganese and cobalt are apparently negative; zinc and cadmium show negative reaction. Copper and lead are poisons; mercury retards; silver, thallium, bismuth, and antimony are poisons, while vanadium, tin, titanium, uranium, and tungsten are not. Gold, platinum, iridium, and osmium do not retard the hydrogenation. Sulfur and selenium are poisons; but tellurium is not to such an extent. Cyanogen and cyanides are strong poisons, as is phosphorus. Boric acid is not negative when added to the catalyzer; but is when present in the oil. Presence of organic matter has no effect if treated at high temperatures.

[49] *J. prakt. Chem.*, **105** (1868), 202.
[50] *Cf.* Senter: *Z. physik. Chem.*, **51** (1905), 702; **72** (1910), 689.
[51] Private communication from Prof. H. S. Taylor.
[52] *Chem. Abstracts*, **15** (1921), 1226.

Harned[53] has shown that the rate of adsorption of chloropicrin by a charcoal which has been cleaned by washing with chloropicrin is much greater than by a charcoal which has not been so cleaned, although the final equilibrium is apparently about the same in the two cases. This is analogous to the evaporation of water when covered by an oil film. The oil cuts down the rate of evaporation very much but has practically no effect on the partial pressure of water at equilibrium.

It is easy to see that a piling up of any of the reaction products on the surface of the catalyst will decrease the reaction velocity if this hinders or prevents the reacting substances from coming in contact with the catalytic agent. This has been observed in the contact sulfuric acid process.[54] The explanation that the decrease in the reaction velocity is due to a decreased adsorption of the reacting substances was first given by Fink,[55] who is the real pioneer in this line. Although the reaction between carbon monoxide and oxygen is practically irreversible, it occurred to Henry,[56] nearly 90 years ago, that the presence of the reaction product, carbon dioxide, might slow up the rate of reaction, and he proved his point by increasing the reaction velocity when he removed the carbon dioxide with caustic potash. Water vapor checks the catalytic dehydration of ether[57] and of alcohol[58] somewhat, and hydrogen cuts down the catalytic dehydration of alcohol. In fact, nickel and copper tend to dehydrogenate substances in the absence of hydrogen and to hydrogenate them in its presence.

Since the poisoning of a catalytic agent is due to marked adsorption, which cuts down the adsorption or the rate of adsorption of the reacting substances, and since the presence of sulfur trioxide, the reaction product, tends to decrease the rate of reaction of sulfur dioxide and oxygen, it follows that an extremely strongly adsorbed reaction product will act as a catalytic poison. In

[53] *J. Am. Chem. Soc.*, **38** (1916), 1145.

[54] Bodländer and Koppen: *Z. Elektrochem.*, **9** (1903), 566; Berl: *Z. anorg. Chem.*, **44** (1905), 267.

[55] Bodenstein and Fink: *Z. physik. Chem.*, **60** (1907), 61; *Cf.* Bunsen: *J. Chem. Soc.*, **25** (1873), 736.

[56] *Phil. Mag.* (3), **9** (1836), 324.

[57] Ipatieff: *Ber.* **37** (1904), 2996.

[58] Engelder: *J. Phys. Chem.*, **21** (1917), 676.

such a case the extent to which the reaction will run will depend on the relative amount of catalytic agent present.[59] If a large amount of catalytic agent be added to a mixture which does not react perceptibly in finite time in the absence of the catalytic agent, the reaction will run to an end or to true equilibrium before the catalytic agent is poisoned completely. If there is only a small amount of catalytic agent, it will be poisoned very early in the course of the reaction and we shall have an apparent equilibrium, reached from only one side, which will vary with the amount of catalytic agent. For any given small amount of catalytic agent we shall get an apparently definite end point; but the value of the end point will vary with the amount of the catalytic agent taken. This is called *autotoxic catalysis.*

At least one case of this sort has been recognized definitely.[60] The amount of splitting of amygdalin by platinum black is small, because one of the reaction products is hydrocyanic acid and this poisons the platinum black. Instead of working with tightly corked flasks, Neilson left the flasks uncorked, and found that the evaporation of the hydrocyanic acid allowed the decomposition to proceed somewhat farther.

Since enzymes are poisoned in the same way that colloidal platinum is, it seems worth while to consider whether autotoxic catalysis will account for some of the peculiarities in enzyme action which have puzzled people. If autotoxic catalysis occurs, the presence of the reaction products will cause a decrease in the reaction velocity even though the reverse reactions are negligible. If the poisoning action of the reaction products is sufficient, we shall get false equilibria if we start with small amounts of the enzymes, while the reaction will run to an end or to true equilibrium if we start with sufficiently large amounts of the enzymes. Both of these cases have been observed;[61] but no one has yet studied the effect of autotoxic catalysis on the reaction velocity. This seems a promising field for investigation.

It has already been mentioned that a sintered catalyst is usually practically inert. The question at once arises whether

[59] BANCROFT: *J. Phys. Chem.*, **22** (1918), 22.

[60] NEILSON: *Am. J. Physiol.*, **15** (1906), 148.

[61] TAMMANN: *Z. physik. Chem.*, **18** (1895), 426; KASTLE and LOEVENHART: *Am. Chem. J.*, **24** (1900), 491; BANCROFT: *J. Phys. Chem.*, **22** (1918), 39.

it is possible to prevent agglomeration of the catalyst and whether there are any accompanying disadvantages. A colloidal solution of Bredig's platinum is fairly unstable, but can, of course, be made more stable by the addition of a protecting colloid, such as gelatin. Ten years ago, Gröh[62] showed that the stabilization of colloidal platinum by gelatin causes a decrease in the catalytic action on hydrogen peroxide, the time for half decomposition increasing nearly tenfold as the amount of gelatin increased from nothing to $\frac{1}{10}$ per cent.

All the subsequent work has confirmed the generalization that we pay for stabilization by a protecting colloid through decrease in the catalytic action. This effect may be masked to some extent if the protective colloid increases the dispersion and, therefore, the surface of the catalytic agent; or if the protecting colloid is itself a catalytic agent.[63]

Iredale[64] has studied the effect of protecting colloids on the catalytic decomposition of hydrogen peroxide by colloidal platinum and finds that the stronger a substance is as a protecting colloid the greater will be its inhibition of catalytic activity. The order of inhibiting effect is: gelatin and glue > egg albumin > sucrose, the last not appearing to affect the reaction at all. One part of gelatin in 20,000,000 of water has a recognizable inhibiting action. Iredale has determined inhibition numbers for these substances, corresponding to the gold numbers. Taking the values for gelatin as 100 in both cases, the gold numbers for gelatin, egg albumin, dextrin, and starch are 100, 20, 0.66, and 0.40, while the inhibition numbers are 100, 20, 1, and 0.33.

Rocosolano[65] found that stabilizing Bredig's platinum with a little gelatin decreases the rate of decomposition of hydrogen peroxide to about one-third. With sodium lysalbinate the rate passes through a minimum with increasing concentration, increasing when the effect of the alkalinity begins to count. There is no minimum with gum arabic and its effect on the reaction velocity is much less than that of an equal weight of gelatin, which is in harmony with Iredale's results.

[62] *Z. physik. Chem.*, **88** (1914), 414.

[63] RIDEAL: *J. Am. Chem. Soc.*, **42** (1920), 749.

[64] *J. Chem. Soc.*, **119** (1921), 109; **121** (1922), 1536.

[65] *Compt. rend.*, **173** (1921), 41, 234.

In all these cases the catalytic agent is coated more or less completely by the protecting colloid. If, however, we fasten the catalytic agent on a rigid support, we shall prevent sintering more or less completely and there will be little or no decrease in the catalytic action.

Taylor and Gauger[66] have found that the adsorptive power of nickel, reduced at 300°, is destroyed if the nickel is heated to 500°. If the nickel is precipitated on kieselguhr or on diatomite brick, it can be heated to, or reduced at, 500° without any change in properties. Since there is always agglomeration when nickel is reduced at 300°, one might reasonably expect that nickel on kieselguhr or diatomite would adsorb more than straight nickel, but it is distinctly a surprise to be told that it will adsorb ten times as much. Pollard[67] found that it is impossible to determine accurately the amount of hydrogen adsorbed by platinum black because the last 30 or more volumes cannot be pumped out except by heating to about 300° and at that temperature the platinum sinters to such an extent that the adsorption changes very much. In other words, adsorption measurements cannot be duplicated satisfactorily with straight platinum black. Platinized asbestos, however, can be heated to 400° without undergoing any change. Mond, Ramsay, and Shields[68] obtained adsorptions of 110 volumes of hydrogen per volume of platinum with their best platinum black; but it is very certain that there were at least 30 volumes of hydrogen which they did not get out and, consequently, did not measure. This is so near to Pollard's value of about 160 volumes that it would not be safe to claim that platinized asbestos adsorbs more or less hydrogen per gram of platinum than platinum black in the same state of subdivision.

Palmer[69] has made reproducible copper catalysts by impregnating cylindrical rods of china clay with copper formate solution. Armstrong and Hilditch[70] have investigated the statement by Kelber[71] that nickel oxide gives a moderately active catalyst when

[66] *J. Am. Chem. Soc.*, **45** (1923), 920.
[67] *J. Phys. Chem.*, **27** (1923), 366.
[68] *Phil. Trans.*, **186** A (1895), 657.
[69] *Proc. Roy. Soc.*, **98** A (1920), 20.
[70] *Proc. Roy. Soc.*, **99** A (1921), 491.
[71] *Ber.* **49** (1916), 55, 1868.

reduced at about 300° and a very poor catalyst when reduced at 450°, whereas nickel oxide deposited upon kieselguhr and reduced at 450° gives a catalyst which is more active than the straight nickel oxide reduced at 300°. This is practically what Taylor and Gauger found. The unsupported nickel sinters and becomes inactive when heated, whereas the kieselguhr does not shrink when heated and holds the nickel in place. It is quite possible that the nickel film is thinner and has more surface when precipitated on kieselguhr than when produced from straight nickel oxide.

Armstrong and Hilditch also discuss the statement that partially reduced nickel oxide is more active than the same oxide when reduced completely. Since a partially reduced nickel oxide will consist of a film of metal coating the unreduced core of the particle, this will behave like a *supported* catalyst, nickel on nickel oxide, and will, therefore, be of the same type, although not of the same degree of activity as nickel upon kieselguhr.

The essential difference between the "supported" catalyst and the "protected" catalyst is that the platinum is on the outside of the asbestos and its rate and power of adsorption are interfered with only at the points of contact between platinum and asbestos, whereas the gelatin is on the outside of the platinum and interferes everywhere with the adsorption of the reacting substances. Quite in accord with this view is the observation by Nelson and Hitchcock[72] that the adsorption of invertase by charcoal or alumina does not necessarily affect the rate at which it inverts sugar. A difference in rate occurs only when the supported catalyst is not distributed uniformly throughout the solution.

While the high temperature,[73] which may occur at the surface of the catalyst in exothermal reactions, tends to make the catalyst sinter, the actual occurrence of the reaction tends to disintegrate the mass and may increase its catalytic action. Bone[74] has shown that a metal surface becomes roughened when so-called flameless combustion occurs at it, and it is well known that a platinum gauze undergoes similar changes[75] when used to

[72] *J. Am. Chem. Soc.*, **43** (1921), 1956.

[73] Zeisberg: *Trans. Am. Electrochem. Soc.*, **36** (1919), 187.

[74] *Phil. Trans.*, **206** A (1906), 1; *J. Franklin Inst.*, **173** (1912), 101.

[75] Parsons: *J. Ind. Eng. Chem.*, **11** (1919), 541.

oxidize ammonia, thereby becoming a more efficient catalyst. Landis[76] claims that the style of surface varies with the impurities in the ammonia and that a platinum gauze must be activated anew if one changes to ammonia from another source, as from Haber ammonia to coke oven ammonia or to cyanide ammonia. There is no independent confirmation of this last statement.

For a more detailed discussion of the theory of contact catalysis, the reader is referred to the Reports of the Committee on Contact Catalysis of the National Research Council, two of which have already been published.[77]

Among the important technical processes involving contact catalysis are the contact sulfuric acid process, the Deacon chlorine process, the Haber ammonia process, the Ostwald nitric acid process, the Sabatier hydrogenation process, and the Welsbach incandescent process (gas mantle).

[76] *Trans. Am. Electrochem. Soc.*, **35** (1919), 300.

[77] BANCROFT: *J. Ind. Eng. Chem.*, **14** (1922), 326, 444, 545, 636; *J. Phys. Chem.*, **27** (1923), 801.

CHAPTER XI

COLLOID CHEMISTRY AND CONTACT CATALYSIS

By

Hugh S. Taylor

Contact catalysis is essentially concerned with a variety of phenomena occurring in the chemistry of reactions at surfaces or interfaces between two phases. The greater the surface or interface the greater is the area in which such chemical reactions occur. Hence, as is now well known, since active contact catalysts display a high ratio of surface to mass, they are employed in the finely divided condition. With the properties of matter in a finely divided condition, colloid chemistry is especially concerned. It, therefore, follows that contact catalysis is an important branch of applied colloid chemistry. Upon theoretical colloid chemistry it can draw for the principles governing the behavior of materials in contact with finely divided substances. The connection between the two may, however, be more intimate, with mutual advantages accruing to each. It is undoubtedly true that on a right understanding of the general principles of colloid chemistry the student of contact catalysis can base much of his reasoning concerning the phenomena with which he deals. On the other hand, the conclusions of the colloid chemist may be amplified and the bases upon which his principles are founded may be broadened by an inclusion of the facts which the study of contact catalysis reveals.

In the majority of contact catalytic actions, the reaction occurs at a solid-fluid interface. Of these reactions, by far the larger proportion are at a solid-gas interface. We may instance, in this regard, many technical catalytic processes, the contact sulfuric acid process, the oxidation of ammonia to nitric acid, the Deacon chlorine process, the vapor phase oxidation of hydrocarbons to yield alcohols, aldehydes, and acids, the hydrogenation

and chlorination of organic vapors, the water-gas reaction—whereby steam and water-gas react to form carbon dioxide and hydrogen—processes of preferential oxidation, and the like. Reactions at solid-liquid interfaces are less common but not less important, as may be illustrated by the industrial hydrogenation of liquid fats at surfaces of nickel or other suitable catalyst. A few cases are known where the interface is a liquid-liquid interface, the Twitchell reagent for fat splitting undoubtedly functioning as an agent for promoting reaction between an aqueous and an oil phase.

All solids tend to adsorb or condense upon their surface, gases, vapors, or liquids with which they are brought in contact. The extent of adsorption varies with the nature and physical conditions of the solid, with the nature of the gas or liquid, their concentrations, and temperature. Classical colloid chemistry has been concerned with adsorption by relatively few adsorbents, charcoal, silica, alumina, glass, wool, rubber, celluloid, asbestos, meerschaum, soils, and a few metals. The study of adsorption from the standpoint of contact catalysis extends enormously the range of both adsorbents and adsorbates.[1] Such extension of the field of study shows that adsorption is a much more inclusive term than formerly believed. It embraces not only physical, capillary condensation phenomena, non-specific in character and paralleling the physical characteristics of the adsorbate, but also definite associations between adsorbent and adsorbate, specific and chemical in character, independent of the physical characteristics of the adsorbate and similar in every respect to ordinary compound formation in stoichiometric proportions. It is these latter adsorptions which are more important in contact catalysis; the former have been discussed almost exclusively in colloid texts.

An index of the range of adsorption is obtained by a study of *poisoning* in contact catalysis, for such cases are to be attributed frequently to adsorption, on the catalyst surface, of a constituent of the surrounding phase which is present only in minute quantities and which is held by the adsorbent so tenaciously that it is with difficulty removed. Certain cases of poisoning are not due to adsorption but to actual chemical reaction with the catalyst, resulting in modification of the chemical nature of the catalyst.

[1] Adsorbate is a convenient designation for any adsorbed substance.

The problem of poisoning has been treated very comprehensively in recent years and has received quantitative study.[2] It will only be necessary, therefore, to indicate some of the typical cases which show the range of adsorption phenomena involved. Faraday proved that traces of grease destroy the catalytic action of platinum. Mond, Ramsay, and Shields showed that mercury behaved similarly. Berliner showed the action of grease on the adsorption of hydrogen by palladium. Schönbein pointed out that the hydrides of sulfur, selenium, tellurium, phosphorus, arsenic, and antimony cut down the activity of platinum. Maxted has demonstrated the decrease in the adsorption of hydrogen by platinum treated with hydrogen sulfide. Maxted also showed that sulfur, arsenic, lead, zinc, and mercury behave similarly towards platinum. Henry showed that a reaction product, carbon dioxide, might retard a reaction by reason of its covering up the surface, and Fink showed that this was true in the case of sulfur trioxide on platinum in the oxidation of sulfur dioxide. Water vapor inhibits the dehydration of alcohol; hydrogen inhibits the dehydrogenation of alcohol at catalyst surfaces. Water vapor inhibits the catalytic activity at iron-molybdenum surfaces in ammonia synthesis, even at 500° C. Oxygen inhibits a variety of reactions at tungsten surfaces at temperatures as high as 2,000°K., as the researches of Langmuir have shown. In solutions, the variety of inhibitors of the decomposition of hydrogen peroxide by platinum or enzymic catalysts well illustrates the range of adsorption on such surfaces.

The quantitative study of adsorption by contact catalysts has been neglected. Only recently has systematic investigation been initiated. The results accumulated, however, warrant energetic prosecution of the investigation. Stock, Gomolka, and Heynemann,[3] made measurements in the course of their investigations on the decomposition of arsine which may indicate some adsorption of arsine on the walls of the containing vessel. Measured pressures of arsine were admitted to glass vessels. The gas was

[2] Bancroft: *J. Phys. Chem.*, **21** (1917), 734; "Applied Colloid Chemistry," McGraw-Hill Book Co., 1921; First Annual Report, Committee on Contact Catalysis: *J. Ind. Eng. Chem.*, **14** (1922), 326, 444, 545, 642; Maxted: *J. Chem. Soc.*, **115** (1919), 1050; **117** (1920), 1280, 1501; **119** (1921), 225, 1280.

[3] *Ber.*, **40** (1907), 532.

then decomposed by heating. The pressure of residual hydrogen was measured. Since

$$2AsH_3 = 3H_2 + 2As$$

the hydrogen pressures thus obtained should be exactly $\frac{3}{2}$ the initial arsine pressure. This was not found, as the following table of results demonstrates.

	Pressure in millimeters		
	At 15°C.	At 25°C.	At 35°C.
p AsH_3	714.2	739.2	764.4
p H_2	1,088.5	1,125.9	1,163.8
$\frac{2}{3}$ (p H_2) − p AsH_3	11.5	11.4	11.5

In the last line is given the difference between the theoretically calculated arsine pressure and that observed initially. Stock and his co-workers ascribed this difference between calculated and observed values to the deviations of arsine from the gas laws. There is a distinct possibility that this deviation is to be ascribed partially to adsorption and partially to the operation of molecular attraction, since at the temperatures employed arsine is some 80 to 100° above its boiling point (−54.8°C.).

Stock and Bodenstein[4] demonstrated that the reaction velocity measurements on the decomposition of arsine on arsenic surfaces were representable by the equation

$$-\frac{d(AsH_3)}{dt} = k(AsH_3)^{\frac{1}{n}}$$

They explained this as due to a distribution of arsine between gas space and surface in accordance with Freundlich's adsorption isotherm.

$$(AsH_3)_{adsorbed} = k(AsH_3)_{gas}^{\frac{1}{n}}$$

They state, however, that the arsine adsorbed is probably too small to measure. This certainly needs experimental test, and is probably not entirely correct.

[4] *Ber.*, **40** (1907), 570.

Fink[5] measured the adsorption of sulfur trioxide on platinum and showed the existence of an approximately unimolecular layer of this gas on the metal at reaction temperatures usual in the contact process of oleum manufacture. This observation was incorporated in the Bodenstein-Fink theory of gas reactions at catalytic surfaces. The reaction velocity was assumed to be determined by the rate of diffusion of the reactant gases through a film of adsorbed resultant, which film was assumed to vary in thickness with the partial pressure of such resultant. As Langmuir has pointed out, with only unimolecular layers possible, this is not satisfactory. Rather, reaction rate is conditioned by the fraction of the surface which is bare of the strongly adsorbed gas (SO_3) under the experimental conditions.

The results of Kuster[6] and Berl[7] are similarly interpretable, the catalysts used being vanadium pentoxide and arsenic pentoxide, the reaction, however, in each case being much slower than with platinum. The researches of L. and P. Wohler and Plüddemann[8] on the catalytic activity of oxides which might form sulfates as intermediate steps in the process, *e.g.*, Fe_2O_3, Cr_2O_3, and those in which this is not likely, Al_2O_3, SiO_2, TiO_2, etc., are worthy of study by the student of adsorption in its relation to catalysis. These workers established the undoubted influence of the state of division of the catalyst on its catalytic activity. They showed that gross particle size was not a measure of catalytic action. They attempted to measure effective surface by studying adsorption of acids, such as acetic and benzoic acids, from solutions by the various catalysts studied. They reach an adverse conclusion in this regard, largely, in the view of the present author, by reason of the specificity of adsorption displayed in the examples studied, a possibility of which the authors were aware but concerning which no large body of available evidence was then to be found.

Langmuir's researches on the clean-up of gases by filaments are too well known to need record here. Those investigations and his studies of catalysis at platinum surfaces[9] have given

[5] *Z. physik. Chem.*, **60** (1907), 1.
[6] *Z. anorg. Chem.*, **42** (1904), 453.
[7] *Z. anorg. Chem.*, **44** (1905), 267.
[8] *Z. physik. Chem.*, **62** (1908), 641.
[9] See especially, *Trans. Faraday Soc.*, **17** (1921), 607, 621.

results from which may be deduced a capacity of such surfaces to adsorb at a maximum a monomolecular film of various gases. Quantitative measurements on platinum, glass, and mica confirm this conclusion.

Systematic study of the quantitative data on adsorption by catalysts when subjected to the action of poisons has been carried out by Maxted in recent years.[10] The decrease in activity caused by the poisons, lead, mercury, zinc, sulfur, and arsenic, is directly proportional to the concentration of inhibitant from zero concentration up to that producing practically complete inactivity. The occlusive power of palladium for hydrogen varies directly as the amount of sulfur present as inhibitant. The amount of lead, as poison, required to reduce the catalytic activity to one-half is very much less than that which reduces the occlusive power to one-half its original value. This may be explained by the fact that, while occlusion is not confined to the surface, catalysis is mainly a surface phenomenon. With metals showing adsorption without marked occlusion, there would doubtless be complete identity between loss of adsorptive capacity and loss of catalytic activity.

Systematic studies of adsorption of a variety of gases by metal catalysts for hydrogenation processes and of metals for ammonia decomposition, of oxides for oxidation processes, and of a few salts have been made in the Princeton Laboratories.[11] The measurements have been made over a wide temperature range and in a few typical cases over a range of pressures. In a few cases, the intimate parallelism between adsorptive capacity and catalytic activity has been traced; Pease's recent studies of the hydrogen-ethylene combination and adsorptions on copper and Benton's recent studies of carbon monoxide and hydrogen adsorptions on oxides as accounting for preferential combustion of carbon monoxide in hydrogen are cases in point. Gauger's

[10] *Loc. cit.*, Ref. 2.

[11] Taylor: *J. Ind. Eng. Chem.*, **13** (1921), 75; Taylor and Burns: *J. Am. Chem. Soc.*, **43** (1921), 1273; Taylor: *J. Franklin Inst.*, **197** (1922), 1; Pease and Taylor: *J. Am. Chem. Soc.*, **43** (1921), 2179; **44** (1922), 1637; Benton: *J. Am. Chem. Soc.*, **45** (1923), 887, 900; Gauger and Taylor: *J. Am. Chem. Soc.*, **45** (1923), 920; Pease: *J. Am. Chem. Soc.*, **45** (1923), 1196; Dougherty and Taylor: *J. Phys. Chem.*, **27** (1923), 533; Jones and Taylor: *J. Phys. Chem.*, **27** (1923), 623.

recent studies of nickel-hydrogen isotherms pave the way to studies of the thermodynamics of such adsorption processes, concerning which practically nothing is now known. Direct measurements of heats of adsorption of gases by catalysts are now being made.

The results so accumulated may now be discussed in detail with particular reference to the aspects of catalysis and adsorption which are involved in such work.

Adsorption Accompanies Catalytic Changes

The general conclusion from the work at Princeton already cited is that adsorption is a condition precedent to catalytic change. The data obtained by Taylor and Burns on hydrogenation catalysts showed marked adsorption of gases which take part in hydrogenation processes. Low adsorptive capacities were found with relatively inert catalysts. Pease studied this relationship in detail with ethylene and hydrogen on copper, showing that high catalytic activity was paralleled by high adsorptive capacity for both gases. Pease further showed that, by suppressing the adsorption of hydrogen by partially poisoning the copper catalyst with mercury, the catalytic activity was likewise suppressed. Adsorption of both reactants is, therefore, a condition precedent to efficient catalysis in this case. Benton showed marked adsorption of carbon monoxide and, to a lesser degree, oxygen by oxide catalysts capable of effecting the combination of these gases. Dougherty and Taylor demonstrated the adsorption of benzene vapors by nickel. Taylor, Benton, and Dew[12] have measured ammonia adsorption on a variety of metals which catalyze the decomposition of ammonia. Taylor and Beebe[13] have shown that hydrogen chloride is adsorbed by the copper chloride catalyst of the Deacon chlorine process.

The Form of the Catalyst and Adsorption

The extent of adsorption per unit weight of catalyst is determined by the method of preparation, distribution on inert supports, or by subsequent treatment of the surface by catalyst poisons or by heat treatment.

[12] Unpublished work.

[13] Unpublished work.

Variation in adsorptive capacity with variation in the methods of preparation may be illustrated from the work on copper, on nickel, and on an oxide such as cupric oxide. These results are strikingly displayed in the following tables.

ADSORPTIONS ON COPPER

Temperature of reduction of CuO, degrees Centigrade	Nature of CuO	Time required for reduction	Adsorption per 100 g. Cu at 0°C. and 760 mm., cubic centimeters		Observers
			H_2	C_2H_4	
250	Ignited nitrate.....	Few hours	0.2	2.85	Taylor and Burns
200	Kahlbaum's granules	30–40 hours	3.0	8.00	Pease
150	Kahlbaum's granules	4 days	15.5	....	Taylor and Dew

ADSORPTIONS ON NICKEL

Temperature of reduction of NiO, degrees Centigrade	Nature of NiO	Time required for reduction	Adsorption H_2 per 100 g. at 25°C. and 760 mm., cubic centimeters	Observers
300	Ex nitrate	12 hours	47	Taylor and Burns
300	Ex nitrate	?	70	Gauger and Taylor
300	Ex nitrate	2 days	130*	Taylor and Beebe

* This catalyst probably more finely divided than the first two.

ADSORPTIONS ON CuO

Nature of CuO	Adsorption per 100 g. CuO at 25°, 760 mm.			
	CO_2	O_2	CO	Observer
Strong ignition of Cu..	0.015	0.005	0.012	Benton
Calcination of nitrate..	0.132	0.000	0.180	Benton
Precipitation of hydroxide	36.2 (0°C.)	1.0 (0°C.)	13.3 (0°C.)	Benton

The effect of a catalyst support on the adsorptive capacity per unit weight of catalyst is well illustrated by the work of Gauger and Taylor with nickel from the calcined nitrate and with nickel spread on a diatomite brick.

Catalyst	H_2 adsorbed per gram of Ni at 750 mm., cubic centimeters						
	25°C.	80.5°C.	175°C.	184°C.	200°C.	218°C.	250°C.
Unsupported Ni	0.69	0.63	...	0.53	...	0.84	
Ni on diatomite	....	....	5.2	....	5.1	....	4.73

The best quantitative data on the effect of poisons on catalyst adsorption obtained in the Princeton work are those obtained by Pease on copper. Adsorptions of hydrogen and ethylene on 100 g. of Cu were made before and after the catalyst was poisoned with mercury, the quantity of poison being estimated at 200 mg.

	Adsorption at 0°C., and 380 mm., cubic centimeters	
	H_2	C_2H_4
Before poisoning	3.25	8.55
After poisoning	0.15	6.70

The striking disparity in the influence of the poison on the adsorptive capacities of the two gases is worthy of study. The hydrogen adsorption is reduced to less than 5 per cent of its initial value. The ethylene adsorption, on the other hand, is still approximately 80 per cent of its initial value. At the present time, we are inclined, taking these data in conjunction with others on the effect of heat to be presented below, to attribute this phenomenon to differing capacities of surface atoms to adsorb hydrogen and ethylene. The mercury vapor, on this hypothesis, would be preferentially adsorbed on those portions of the surface which have hydrogen-adsorbing capacity.

Heat treatment of an active catalyst preparation is now our standard method of preparing catalysts with controlled adsorptive capacity or catalytic activity. From a variety of experiments, we may choose the following as indicative of the effect produced by heat treatment.

Catalyst	Heat treatment	Adsorption at 0°C. and 760 mm., cubic centimeters		Observer
		H_2	C_2H_4	
A. Active Cu, 100 g.	No heat beyond reduction of oxide at 200°C.	3.70	8.45	Pease
B.	A. heated to 450°C. for 1.5 hours.	1.15	6.85	Pease
C. Active Ni, 27 g.	Obtained by reduction of oxide at 300°C.	35.00	....	Beebe
D.	D. heated at 400°C. for 4 hours.	16.00	....	Beebe

The same abnormal depreciation of the hydrogen adsorption on copper is to be noted here as in the poisoning experiments. This evidence we would interpret thus: A smaller fraction of the surface is required for adsorbing hydrogen than for adsorbing ethylene. The greater adsorptive force required by surface atoms in order to hold hydrogen is, in our view, to be regarded as possessed by those atoms in the surface which have a greater degree of freedom from the normal crystal lattice of the solid catalyst. These atoms have a lesser fraction of their electron shells surrounded with neighboring copper atoms. They, therefore, possess a greater surface energy. They would also possess a higher vapor pressure. With the moderate heat treatment accorded to the catalyst in the above-mentioned cases, these atoms distill to positions of lesser surface energy more readily than do atoms of less freedom in the solid lattice. It is these atoms of high surface energy which will be most affected by heat treatment; they should be the preferred positions of attachment of catalyst poisons.

The Specificity of Catalytic Adsorption

Freundlich points out[14] that:

Since, in adsorption by charcoal, the physical characteristics of the adsorbed gas are of far more importance than the specific effect between gas and adsorbent, it is not remarkable that also with adsorption by different adsorbents the influence of the special properties of the adsorbent is strongly suppressed (*stark zurucktritt*). It can be said with a certain approximation that oftentimes gases are adsorbed, independently of the nature of the adsorbent, in the order of their compressibilities.

This thesis is entirely inapplicable to catalytic adsorption. The ratio $\frac{\alpha_1}{\alpha_2}$ for the adsorption of two gases by adsorbents A, B, C, etc., which, on the basis of Freundlich's statement, would be approximately constant for each adsorbent, A, B, C, etc., may vary quite widely for catalytic adsorbents. The large differences in the ratio of adsorption of carbon monoxide at 0°C. to carbon dioxide at 0.°C., obtained by Benton, show the specific nature of carbon monoxide adsorption at this temperature for a variety of oxide catalysts.

$\frac{\alpha CO}{\alpha CO_{2(0°C.)}}$	Hopcalite	CuO	MnO_2	Fe_2O_3	V_2O_5	SiO_2
	0.72	0.37	0.22	0.09	0.14	0.08

The same ratio at 25°C. for a few metallic catalysts is obtainable from Burns' measurements.

$\frac{\alpha CO}{\alpha CO_{2(25°C.)}}$	Cu	Co	Fe	Pd	Pt Black
	10.0	3.6	2.8	288	10.6

It is very evident, since this ratio varies from 0.1 to 300, that the Freundlich relation is entirely untenable for such cases as we are dealing with here. It has only a very circumscribed applicability, namely, to chemically inert adsorbents and to easily liquefiable gases. A most striking case of the specific behavior of catalytic nickel is to be found in Freundlich's book (page 203) in

[14] "Kapillarchemie," 2nd ed., 1922, p. 178.

his discussion of some unpublished work by Zisch on the decomposition of nickel carbonyl at nickel surfaces. As Freundlich points out, one might expect, on the basis of the higher critical temperature of nickel carbonyl as compared with carbon monoxide, a much higher adsorption. Actually, carbon monoxide, even in minute quantities, exerts a powerful retarding action on the decomposition, indicating marked preferential adsorption. Our present knowledge with respect to the structure of nickel carbonyl and its stable configuration on the basis of the Lewis-Langmuir-Kossel theory of structure immediately suggests the chemical reasons for this specificity of adsorption, unexplainable on the basis of physical characteristics. Other striking variations in ratio of adsorbed gases are to be found in the records of the Princeton work. Consideration of the preceding section on the influence of catalyst poisons and of heat treatment on adsorptive capacity will show, furthermore, that the ratio of adsorption of gases by a single catalyst is also variable with variation in the method of preparation and of treatment of the catalyst. The rule as to non-specificity of adsorbents must be discarded when cognisance is taken of the data on catalytic adsorbents.

Specificity of Adsorption and Specificity of Catalytic Activity

The influence of specific adsorption in determining specific catalytic activity is best demonstrated by work dealing with the preferential catalytic combustion of carbon monoxide admixed with hydrogen. As is well known, metallic oxides may be used to catalyze the combination of carbon monoxide and oxygen present in equivalent concentrations in a large excess of hydrogen. The mechanism of this preferential oxidation is at once apparent from the adsorption ratio of the two gases at atmospheric pressure on various oxides at $-79°$C., as determined by Benton.

$\frac{\alpha CO}{\alpha H_{2(-79°)}}$	Hopcalite	MnO_2	CuO	Co_2O_3	Fe_2O_3	V_2O_5	SiO_2
	33	100	34	19	35	17	28

For exact comparison with preferential combustion data, adsorptions at low partial pressures of carbon monoxide should be compared with those of hydrogen at approximately atmospheric pressure. The results cited, however, show marked preferential adsorption of carbon monoxide. With metals, the preferential nature of the combustion process is less pronounced. With nickel and platinum, the hydrogen is freely consumed; with copper, a fair preferential combustion may be attained. Note the following data on adsorption ratios of the two gases at various temperatures and atmospheric pressure, and contrast them with the oxide data.

$\frac{\alpha CO}{\alpha H_2}$	Ni	Pt Black	Cu
	0.87 (184°)	3.3 (100°)	12

The data cited are also of interest in connection with the problem of specificity of adsorbent discussed in the preceding section.

Variation of Adsorption with Pressure and the Heat of Adsorption

As is well known, the variation of adsorption with pressure on adsorbents, such as charcoal, is approximately given by the Freundlich equation

$$\alpha = kc^{\frac{1}{n}}$$

where α is the amount adsorbed, and k and n are constants, the latter being always equal to, or greater than, unity.

The data on the variation of adsorption with gas pressure with metallic catalysts as adsorbents are few; some of these, however, show striking characteristics. Gauger and Taylor's data on the adsorption isotherms of hydrogen on nickel are the most completely studied thus far. The curves obtained at a variety of temperatures from 25° to 305°C. show the characteristic shape of normal adsorption isotherms, so far as absence of discontinuities indicative of compound formation are concerned; they show, however, this distinction, that at a certain pressure at

each temperature a definite saturation capacity of the surface is apparently reached. This saturation capacity is reached at very low partial pressures, 40 mm. at 25°C., and approximately 250 mm. at 305°C. Beyond these pressures, further increase in gas pressure up to atmospheric pressure (*i.e.*, $^{760}/_{40}$ = 19 fold increase in pressure at 25°C.) adds to the amount of gas adsorbed so little as to be within the error of measurement. The same observation is true in the recent results of Pollard,[15] employing hydrogen, and, to a less extent, carbon monoxide on platinum. The amount of adsorbed hydrogen in this case does not sensibly increase beyond a gas pressure of 100 mm. Pease's data on the adsorption of hydrogen by copper show a similar if less pronounced attainment of saturation capacity. The adsorption of hydrogen at 380 mm. pressure was 90 per cent of that at atmospheric pressure. Similar behavior with respect to carbon monoxide on copper is shown in some unpublished measurements of Jones and Taylor on the adsorption isotherms of carbon monoxide and carbon dioxide on copper at 0° and 80°C. Published work on adsorbents of the charcoal type has not indicated the attainment of saturation capacity of the surface, even at pressures well beyond atmospheric pressure. A further distinction is also noticeable. Gauger and Taylor's results show that the adsorptive capacity of hydrogen on nickel at saturation is, at 305°C., as much as 60 per cent of the saturation capacity at 25°C. Some recent data obtained by Dew on copper show adsorptions of hydrogen in the ratio of 10 to 8.7 at 0° and 110°C. and atmospheric pressure. Contrast this with the data concerning adsorption on charcoal. The adsorption of carbon monoxide on charcoal at 400 mm. and 46°C. is only 8 per cent of that at −78°C., this temperature interval being about the same as that obtaining in Dew's case and less than one-half of that recorded above with nickel and hydrogen. The adsorption of carbon dioxide on charcoal at 150°C. and atmospheric pressure is less than 7 per cent of that at −78°C. These striking differences, both in the pressures at which saturation is attained and in the variation of adsorption with temperature, are undoubtedly of fundamental importance in the study of catalytic adsorbents.

[15] *J. Phys. Chem.*, **27** (1923), 365.

Data on adsorption isotherms may be utilized to evaluate the heat of adsorption of gases on the adsorbent surface. Gauger and Taylor, using the minimum pressures at which saturation is reached at the several temperatures, and substituting these in the equation

$$\lambda = 4.57 \frac{T_1 T_2}{T_2 - T_1} \log \frac{P_2}{P_1}$$

obtained a value for λ the heat of adsorption of 2,500 cal. This calculation is in error, since the equation should be applied (see Freundlich, second edition, page 182) to the pressures P_1 and P_2 at which *equal* amounts of gas are adsorbed. The data of Gauger and Taylor do not lend themselves readily to such computations if accuracy is desired, as the pressures at which equal amounts of gas are adsorbed at different temperatures are small and consequently most liable to error. From the best available data, however, calculated in the correct manner, a value for the isosteric heat of adsorption of 15,000 $\pm$ 3,000 cal. was obtained.

In the meantime, a direct determination of the heat of adsorption of hydrogen on nickel has been carried out by Beebe and Taylor. We shall report elsewhere[16] the details of these measurements. It will suffice here to say that, on a freshly prepared, highly active sample of nickel, a heat of adsorption equal to 13,500 cal. per mol was obtained. It is to the magnitude of this value that we wish to draw special attention.

It is at once evident that there is a wide deviation in this case between the heat of adsorption and the heat of liquefaction of hydrogen, which latter cannot be much greater than 450 cal. per mol. Further, a little consideration will show that it is to this abnormally high heat of reaction that the characteristic curves of the nickel-hydrogen isotherms are to be attributed. From the isotherms it may be shown that, with a given sample of nickel, 8.7 cc. of hydrogen were adsorbed at 25°C. and 40 mm. pressure. Utilizing the directly observed value for λ = 13,500 cal., we may now calculate at what pressure 8.7 cc. of hydrogen will be adsorbed at any other temperature. Thus, for T = 184°C., we have

$$13{,}500 = \frac{4.57 \times 298 \times 457}{(457 - 298)} \log \frac{P_2}{40}$$

[16] *J. Am. Chem. Soc.*, **46** (1924), 43.

whence $P_2 = 71{,}300$ mm., approximately; or, somewhat less than 100 atmospheres is the pressure at which the nickel surface will be covered with 8.7 cc. of hydrogen gas at 184°C. But Gauger's measurements show that already at 150 mm. pressure 8 cc. of gas are adsorbed. A further 100 atmospheres, therefore, only produce an additional adsorption of 0.7 cc., a result in entire agreement with that found experimentally, namely, that within the range 150 to 760 mm. at 184°C., and in the range 40 to 760 mm. at 25°C., the adsorption was, within the error of measurement, constant. In a similar manner, it may be calculated that at 305°C. it would require some 2,540,000 mm. or some 3,000 atmospheres gas pressure to cover the surface with 8.7 cc. adsorbed gas. In other words, it is to the abnormally high heat of adsorption that the observed independence of adsorption with pressure is to be attributed. In confirmation of this observation, it is interesting to note that Mond, Ramsay and Shields' measurements of the heat of adsorption on platinum of hydrogen gave a value of 13,760 cal. per mol of adsorbed gas. Langmuir estimates the heat of adsorption of carbon monoxide on platinum at 30,000 cal. These high values are consonant with the shape of Pollard's curves for the adsorption of these gases on platinum. The data of Jones and Taylor on carbon monoxide are suggestive of the same high value for heat of adsorption. A calculation from two pairs of isosteres gives a value of 6,500 $\pm$ 300 cal. This is markedly higher than the value for the heat of liquefaction, which, on the basis of Trouton's rule, $\lambda = 22T_B$, should be $22 \times 81 = 1{,}780$ cal. It is interesting to note that from Pease's data on ethylene, a gas whose isotherm at 0°C. is much more reminiscent of isotherms on charcoal, the value deduced from the isosteres at 0 and 20°C. (480 and 760 mm., 5.5 cc. adsorbed) for the heat of adsorption may be calculated to be 3,750 cal., which is exactly what would be deduced from Trouton's rule for heat of vaporization. From the isosteres at lower pressures, higher heats of adsorption are calculable. From the isostere for 3.85 cc. (200 and 380 mm. approximately) the calculated value is about 5,100 cal.

It is evident, therefore, that in the investigation, on the one hand, of adsorption isotherms of various catalyst-gas systems and, on the other hand, in the direct determination of heats of

adsorption, we have two powerful instruments with which to examine further into the mechanism of catalytic action. Both of these instruments are being intensively employed.

We regard the slight variation of adsorption with pressure after the initial strong adsorption at the lower partial pressures in several of the cases studied as the strongest evidence in favor of Langmuir's theory of a unimolecular layer. There is evident little or no tendency to build up layers of adsorbed molecules on such surfaces. Indeed, the results at the higher temperatures suggest that considerable pressures may be necessary before even the surface is covered with a layer one molecule deep. With ethylene and ethane at 0°C., in Pease's experiments, and with carbon dioxide at 0°C. in Jones and Taylor's experiments with copper, there is possible evidence of liquefaction phenomena in addition to the specific adsorption of gas-solid.

It is interesting to obtain evidence of this from another direction in which the difficulties associated with the definition of the surface are absent. This is so in a recent publication by Iredale,[17] who has investigated the adsorption of methyl acetate vapor on liquid mercury by determining the change of surface tension of mercury with varying partial pressures of the vapor. The following table shows this variation from zero pressure to 227 mm., the saturation pressure at the temperature employed (26°C.).

V.P.	0	19	62	109	137	157	227 mm.
γ	472	444	423	419	418	417	412 dynes/ 370 sq. cm.

It will be noted that from 62 mm. up to the saturation pressure, there is only a slight variation in surface tension with change in vapor pressure. This points to the attainment of an approximately monomolecular adsorbed layer at less than one-third of the saturated vapor pressure. Iredale has calculated the amount adsorbed at 62 mm. as of the order of 4.5×10^{-8} g. of methyl acetate per square centimeter of mercury. This is equivalent to

[17] *Phil. Mag.* **45** (1923), 1088.

0.37×10^{15} molecules per square centimeter, or to an area of approximately 27×10^{-16} sq. cm. per molecule, which is comparable with that deduced by Langmuir for the area occupied by such esters when oriented at a water surface.

Adsorption and Catalytic Activity

This abundance of evidence as to the existence of adsorption with catalytic materials must not, however, be taken to imply that the existence of adsorption is the sole criterion of catalytic change. On the contrary, abundant evidence is forthcoming that adsorptive capacity is no sufficient criterion of catalytic efficiency. The poor catalytic properties of charcoal and silica gel constitute one such piece of evidence. Furthermore, the specificity of catalysts, even when adsorptive capacity for reactants and resultants is demonstrated, is yet another line of evidence. All of the metals listed in the subjoined table show measurable adsorptions of the reacting gases in the reactions indicated. They display, however, the marked divergencies which are noted in the table.

Reaction	Catalysts	Non-catalysts
$CO + 3H_2 = CH_4 + H_2O$	Ni, Co, Fe, Pd	Cu, Pt
$2CO = CO_2 + C$	Ni, Co, Fe	Cu, Pt
$C_6H_6 + 3H_2 = C_6H_{12}$	Ni	Cu

It is elsewhere suggested that orientation of the adsorbed molecules may account in part for such specificity. It seems possible to picture the second reaction occurring if the metal-gas linkage be Me−CO in the catalytic reactions and Me − OC in the non-catalyzed reactions. As yet, there seems to be no evidence either way in this regard.

While, however, it is certain that orientation may in some cases be called in to assist in the explanation of mechanism, it is equally certain that orientation in adsorption is not sufficient to account for all such specificity of catalytic action. It will be generally agreed that such organic molecules as formic acid or the

esters will be adsorbed to the catalyst at the $-C = O$ grouping. And yet, as the researches of Adkins have effectively demonstrated, it is possible to alter, almost at will, the nature of the decomposition produced in a body so adsorbed by suitable alteration of the catalyst employed.

The conclusion seems inevitable that the cause of specificity lies in the disturbance exercised by the process of adsorption on the configuration of the adsorbed molecule. We have seen already that there are evidences of profound change in the abnormally high thermal magnitudes associated with certain typical activating adsorptions. The adsorption of hydrogen by nickel, as the heat of adsorption reveals, is no such small disturbance of the electronic forces of the molecule as is involved in a simple condensation process. The disturbance caused is more deep-seated. When no such deep-seated disturbance of the molecule occurs, as in the case of adsorption by charcoal and silica gel, values more closely approximating heat of condensation obtaining, little catalytic activity is manifest.

We look, therefore, towards an explanation of catalysis in the influence exercised by the adsorbent on the configuration of the adsorbate. By the adsorption, the whole electron field of the adsorbed molecule must be altered. The extent of this alteration must be revealed in part in the measurement of the energy changes involved. The actual alteration achieved must be determined by the nature of the adsorbent. We can exemplify this in the comparatively simple case of the decomposition of ammonia at metal surfaces where variation in the nature of the decomposition and in the ease of decomposition is determined by the nature of the metal constituting the surface. At a sodium surface sodamide is formed and hydrogen set free. At copper surfaces ammonia is freely adsorbed but with difficulty dissociated. With nickel, and still more so with iron and with iron-molybdenum, dissociation into elementary constituents occurs. Undoubtedly, the interplay of electrons as a result of the adsorption association is responsible for the divergencies.

In the more complex cases of the organic molecules, the nature of the decomposition products must be determined by the nature of the changes in configuration caused by the attachment. That such attachments are capable of effecting a pronounced change

throughout the molecule is well known to all chemists in a somewhat different guise. The introduction of a chlorine atom into the final methyl group of all the fatty acids exercises an influence on the molecule which is transmitted throughout the length of the hydrocarbon chain and is revealed in the extent of dissociation of the acid. Thus, the acidic hydrogen of chloracetic acid is much less firmly attached to the anion than is the hydrogen ion in acetic acid, as is revealed by its pronouncedly greater degree of dissociation. The same is true with propionic, butyric, and the higher acids. On the other hand, the substitution of an $-NH_2$ grouping for $-Cl$ has the opposite effect. It does not seem unreasonable, therefore, to postulate that the nature of the catalyst should exercise an influence on the adsorbate which is transmitted throughout the length of the adsorbed molecule; so that, in the one case, for example, with formic acid, the nature of the linkage should promote a $O = C\begin{matrix}H\\OH\end{matrix}$ split and in the other case a $O = C\begin{matrix}OH\\H\end{matrix}$ split.

Adsorption by Catalysts in Liquid Systems

This field is just beginning to be explored. Rideal[18] in a study of the hydrogenation of the sodium salts of cinnamic and phenyl propiolic acids in aqueous solution at a palladium sol surface has attempted to demonstrate the extent of such adsorption. He showed that a sol protected by 0.2 per cent gum arabic undergoes aggregation when treated with the sodium salts. Of a sol so aggregated, 10 mg. were filtered through a small filter and washed into a tube connected to a hydrogen burette. The aggregated sol and filter paper adsorbed 4.35 cc. of hydrogen at 25°C. A duplicate filter paper through which 0.1 N sodium phenyl propiolate has been filtered required a further 1 cc. of hydrogen. Of the sol untreated with salt, 10 mg. adsorbed 1.53 cc. hydrogen. Hence, Rideal concludes, the sol had adsorbed salt equivalent to $4.35 - (1 + 1.53) = 1.82$ cc. hydrogen. This corresponds

[18] *Trans. Faraday Soc.*, **19** (1923), 90.

approximately to 1 molecule of salt to 2 atoms of palladium, which may or may not be significant.

A number of investigations on preferential hydrogenation in liquid systems point definitely to the existence of preferential adsorption of one constituent of a mixture by the catalysts of hydrogenation. Moore, Richter, and van Arsdale[19] showed that the more unsaturated glycerides were hydrogenated preferentially to the glycerides containing only one double bond. Quite recently, Richardson, Knuth, and Milligan[20] have confirmed this conclusion, showing that the preferential nature of the process is even more pronounced than had been previously believed. A newer method of analysis of the hydrogenated product revealed, in a typical case, the following percentages of saturated, oleic and linolic acid glycerides in the oil before and after hydrogenation.

Cottonseed oil	Percentages		
	Saturated	Oleic	Linolic acids
Before hydrogenation	22.7	27.5	49.8
After hydrogenation	24.0	67.1	8.9

It is evident that, in this experiment, the hydrogenation was, practically exclusively, hydrogenation of linolic acid glycerides and negligible hydrogenation of oleic acid compounds. This would indicate almost exclusive adsorption of the more highly unsaturated glycerides at the nickel surface. The authors found that the selectivity of the hydrogenation appears to be more marked with increasing amounts of catalyst and with increasing temperature up to an optimum in the neighborhood of 200°C. Quantitative measurements on preferential adsorption should prove very interesting in this case. As Bancroft has already pointed out,[21] there are almost no quantitative data on selective adsorption. An intensive study of the field will be fruitful alike to colloid chemistry and contact catalysis.

[19] *J. Ind. Eng. Chem.*, **9** (1917), 541.

[20] A. C. S., September meeting, 1923, Milwaukee, Wis.

[21] "Applied Colloid Chemistry," McGraw-Hill Book Co., 1921, p. 73.

CHAPTER XII

SENSITIZATION BY MEANS OF HYDROPHILE SOLS

By

HERBERT FREUNDLICH

One occasionally meets with the complaint that, although colloid chemistry is undoubtedly of the greatest importance in many biological and technical problems, yet its employment does not result in as rapid a solution of these problems as might be expected. We forget, however, that most of the applications of colloid chemistry deal with questions upon which little experimental work has been done. In the laboratory we generally use sols and gels which contain essentially one type of micelle only. This produces a decided simplification of the exceedingly complicated phenomena of colloid chemistry. But in natural and industrial processes we deal, in nearly every case, with systems in which two or more types of colloidal particles are present, such as blood, lymph, bread, cheese, wood, or soil. This renders our problems much more difficult for the technic necessary in separating particles of different nature from one another has scarcely been developed. Furthermore, we have only recently begun to understand the reciprocal influences exerted by the particles of such systems.

As one example of such reciprocal influence, the protective action exerted by many hydrophile sols on a hydrophobe sol is well known and has found many applications. When gelatin is added to a gold sol (prepared by the addition of formaldehyde to a solution of gold chloride), it becomes much more difficult to precipitate by the addition of electrolytes.[1] For example, in a gelatin-free sol a concentration of 20 millimols of sodium chloride is sufficient to cause a change from red to blue within 5 minutes. But when the gold solution contains about 0.01 mg. of gelatin to 0.6 mg. of gold, no coagulation is observed, even with a concentration of 200 millimols of sodium chloride.

Many other hydrophile sols, as albumin, casein, gum arabic, and dextrin, act in the same manner. Not only metal and sulfide sols, but also colloidal dyestuffs, as Congo red, can be protected. The particles of the hydrophile sol must always be present in a certain excess over that of the hydrophobe in order that a protective action may take place. For smaller concentrations of the hydrophile sol, a surprising phenomenon often occurs, in that the particles of the hydrophobe colloid are either coagulated or made more sensitive to the effect of electrolytes. A smaller concentration of a given electrolyte is then required for coagulation than is necessary in the absence of the hydrophile sol.

This increased sensitivity produced by hydrophile sols has been known for a long time,[2, 3, 4] but only recently has it been investigated closely and employed for various purposes. In the following pages an attempt is made to assemble our present knowledge of the nature and use of this phenomenon.

The Nature of the Process

The increased sensitivity of ferric oxide sols after addition of albumin, which was discovered by Pauli and Flecker,[4] has been studied more closely by Brossa and Freundlich.[5] This pair of colloids affords a good example of the process in question.

The customary ferric oxide sol is used, obtained by the dialysis of a ferric chloride solution containing ammonium carbonate. After mixing this with a carefully prepared solution of electrolyte-free albumin, a solution is obtained which is apparently the same as that of an ordinary ferric oxide sol of the same concentration. One difference is that the albumin ferric oxide sol may appear a trifle more turbid, in which case it will foam, a behavior not exhibited by the pure ferric oxide sol. In contrast to the latter, it is much more sensitive towards electrolytes, being coagulated by far smaller concentrations than the pure water sol.

The experiments in Table I were carried out in the customary manner. To 5 cc. of the albumin ferric oxide sol, 1 cc. of electrolyte solution was added. After vigorous shaking, the mixture was allowed to stand for 2 hours and the extent of coagulation noted. The data refer to the electrolyte concentration after

dilution of the sol. Experiments were conducted at room temperature.

TABLE I

Albumin sol dialyzed for 5 days. Concentration 6.72 g. per liter; 50 cc. mixed with 4.5 cc. ferric oxide sol containing 17.0 g. ferric oxide per liter. Pure ferric oxide sol used for comparison: 50 cc. water and 4.5 cc. ferric oxide sol.

Concentration of NaCl, millimols per liter	Albumin ferric oxide sol	Pure ferric oxide sol
0.78	Clear, not flocculated	Clear, not flocculated
1.56	Very turbid	Clear, not flocculated
3.13	Completely flocculated	Clear, not flocculated
6.25	Completely flocculated	Clear, not flocculated
12.50	Completely flocculated	Clear, not flocculated
25.00	Turbid flocculated	Clear, not flocculated
50.00	Somewhat turbid	Completely flocculated
100.00	Somewhat turbid	Completely flocculated

The coagulation values for the mixed sols lie between 0.78 and 1.56 millimols, or about 1.2 millimoles, while that of the pure sol is about 37 millimols. Such experiments can be readily duplicated. The behavior of the albumin ferric oxide at higher concentrations of sodium chloride will be discussed briefly further on. At first it plays no part in the increased sensitivity of the sol.

The albumin ferric oxide sol as well as the untreated ferric oxide sol is charged positively and its micelle travel to the negative electrode. The ease of coagulation depends on the nature of the anion, its valence,[6] and its capacity for being adsorbed. As a rule, the increased sensitivity manifests itself more strongly with the weaker coagulating monovalent anions, such as Cl, NO_3, etc. With the more strongly coagulating polyvalent anions, the effect is less pronounced and is sometimes entirely absent. Table II shows the degree of increased sensitivity produced by some heavy anions.

TABLE II

For sodium chloride and potassium sulfate the same sol was used as in Table I. For the other two a sol prepared as follows was employed: albumin sol dialyzed 7 days; concentration 7.8 g. per liter; 50 cc. mixed with 4 cc. of the same ferric oxide sol used in Table I.

Electrolyte	Coagulation value of albumin ferric oxide sol	Coagulation value of pure ferric oxide sol
Sodium chloride.....	1.20	37.00
Sodium salicylate.....	0.29	2.30
Sodium urate.....	0.18	0.25
Potassium sulfate.....	0.29	0.59

For the production of this phenomenon it is necessary in most cases that the sol be thoroughly free from electrolytes. In the research described above this was accomplished by a long period of dialysis, the albumin solution being protected from bacterial action by a layer of toluene. A procedure that can be recommended as much more convenient and rapid is that worked out by the Elecktro-Osmose Gesellschaft.[7] An electrolysis cell of stoneware with a rectangular cross-section made in three separate parts *A*, *M*, *K*, Fig. 1, is used. The apparatus is held together by a screw. The middle part *M* is covered on both sides by membranes so that the apparatus is divided into three cells. The sol is placed in the middle cell between the membranes, and the electrodes are placed in the two outer cells. The cells are filled with pure water constantly renewed by a suitable device. It is important that different membranes be used on the two sides, a positive at the anode and a negative at the cathode. Chromgelatin, tanned by exposure to light, is a suitable positive membrane. Parchment paper can be used for the negative membrane. If two negative membranes are used, the middle layer becomes acid on electrolysis, while with two positive membranes it becomes alkaline. This probably depends on the change of concentration accompanying flow through membranes as studied by von Bethe and Toropoff.[8] The anode is a gauze of platinum wire, the cathode one of brass wire. The electrolysis is carried out at a

potential of 120 to 240 volts. By use of an additional resistance the current is never permitted to exceed 2 amp. This holds the temperature below 45°. If the middle layer is kept in constant motion it is possible to make the diluted serum (the serum is diluted five to ten fold) as free from electrolyte in the course of 10 to 40 minutes as it could be obtained after a week of analysis.

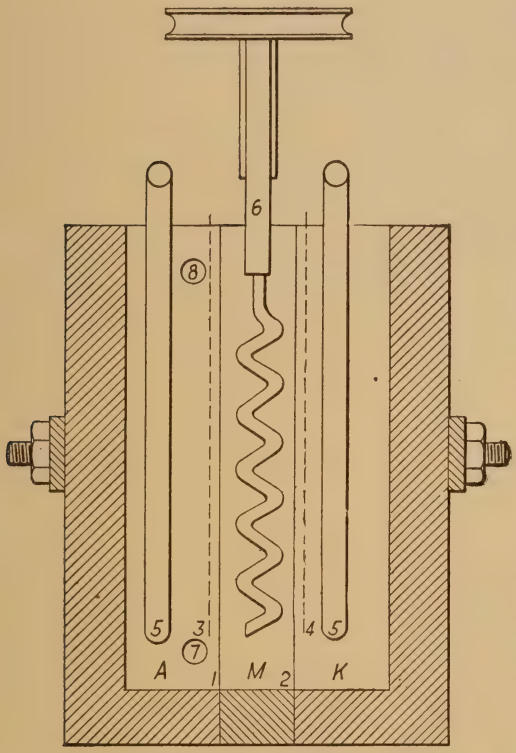


FIG. 1.—Apparatus for electrolytic purification of serum. *M*, Middle cell; *A*, anode space; *K*, cathode space; 1, chrom-gelatin membrane; 2, parchment membrane; 3, platinum gauze; 4, brass gauze; 5, cooling coil; 6, stirring device; 7, inflow for distilled water; 8, outflow for distilled water.

The magnitude of the increased sensitivity depends on the ratio of albumin to ferric oxide. With increasing ratio of albumin to ferric oxide the sol becomes more sensitive. In the following paragraphs are given a series of experiments with sols containing

a constant percentage of albumin but with increasing ferric oxide content.

With increasing content of ferric oxide the behavior of the mixture approaches that of the pure ferric oxide sol. This is shown more distinctly in Fig. 2. The abscissae represent the concentration of sodium chloride, the ordinates the degree of

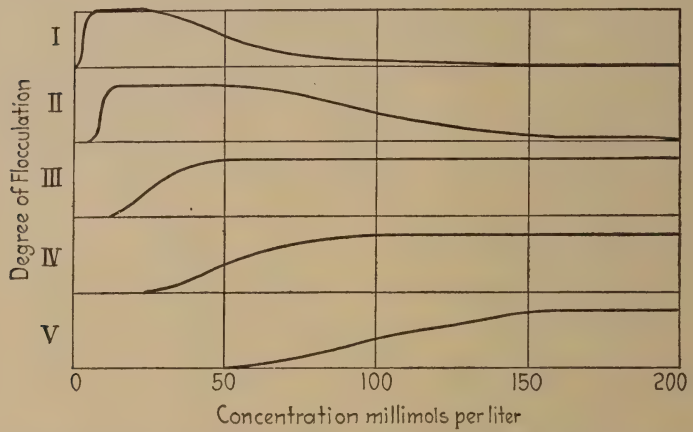


FIG. 2.—The concentration of sodium chloride required to produce flocculation of an albumin sol sensitized with increasing amounts (I to V) of ferric oxide sol. (*Cf.* Table III.)

coagulation measured in arbitrary units. The Roman numerals refer to the corresponding numbers in Table III.

With high albumin content, the strong peptizing action of sodium chloride in high concentration becomes noticeable. The peptization is associated with a transfer of electricity, such as occurs with globulin suspensions.[9] In both cases the anion concentration which produces the peptization is less the greater the valence of the anion and the more readily it is adsorbed.

TABLE III

Albumin sol dialyzed for 7 days. Concentration 7.58 g. per liter; 50 cc. mixed with increasing amounts of the same ferric oxide sol used in Table I. The pure ferric oxide sol used for comparison contained 50 cc. water and 25 cc. ferric oxide sol.

Concentration of NaCl, millimols per liter	50 cc. albumin sol mixed with				
	4 cc. 1	7 cc. 2	15 cc. 3	25 cc. 4	Pure ferric oxide sol 5
1.56	Clear, not flocculated				
3.13	Turbid	Clear, not flocculated			
6.25	Completely flocculated	Clear, not flocculated	Clear, not flocculated		
12.50	Completely flocculated	Completely flocculated	Clear, not flocculated	Clear, not flocculated	
25.00	Completely flocculated	Completely flocculated	Turbid	Clear, not flocculated	
50.00	Turbid, partly flocculated	Completely flocculated	Completely flocculated	Turbid	Clear, not flocculated
100.00	Scarcely turbid	Turbid	Completely flocculated	Completely flocculated	Turbid
200.00	Clear, not flocculated	Scarcely turbid	Completely flocculated	Completely flocculated	Completely flocculated
1,000.00	Clear, not flocculated	.....	Completely flocculated	Completely flocculated	Completely flocculated

The albumin ferric oxide sol, without addition of electrolyte, is not noticeably less stable than the pure sol. In some cases the hydrophile sol alone can coagulate the hydrophobe. This occurs when a silver sol is mixed with increasing amounts of gelatin.[10] From the following data it can be seen that very small concentrations of gelatin produce increased sensitivity, while a definite larger concentration causes flocculation without any addition of electrolyte.

TABLE IV.—COAGULATION VALUES FOR STRONTIUM NITRATE

Concentration of gelatin, milligrams per liter	Concentration of silver sol in grams per liter		
	0.375	0.75	1.5
0	0.55	0.55	0.55
5	0.46	0.50	
10	0.22	0.42	0.52
15	Flocculated without electrolyte		
20	Flocculated without electrolyte	0.28	0.46
30	Protected	Flocculated without electrolyte	
40	Protected	Flocculated without electrolyte	0.23
50	Protected	Protected	0.14
60	Protected	Protected	Flocculated without electrolyte
80	Protected	Protected	Flocculated without electrolyte
100	Protected	Protected	Protected

This table also shows that the behavior of silver sols is similar to that of albumin ferric oxide sols, the increased sensitivity being the more pronounced the greater the ratio of hydrophile sol to hydrophobe sol. The negative silver sol of Carey Lee acts like the positive ferric oxide sol. With a certain larger concentration of gelatin a protective action appears. The greater the concentration of the original hydrophobe sol, the higher the concentration of the hydrophile sol at which protective action begins. This demonstrates in a striking manner the common experience that one and the same hydrophile sol may act as a protective colloid in high concentrations, while in low concentrations it may produce an increase in sensitivity. For this reason one cannot properly speak of a substance as a protective colloid. It is necessary to specify under what conditions, especially of concentration, it exhibits such behavior.

No precise statement can be made of the properties that must be possessed by a pair of colloids in order to exert such reciprocal influences. Of the pronounced hydrophobe sols, Donnau's acid gold sol[11] (gold chloride solution reduced by carbon monoxide) resembles closely the silver sol of Carey Lee. Ganz[12] obtained a sudden change of properties by use of gelatin. Freundlich and Loening[10] were able to demonstrate exactly, as in the case of the silver sol, the same series of phenomena—*i.e.*, an increased sensitivity with small concentrations of gelatin, coagulation by a slightly larger concentration, and with still larger concentrations a protective action.

Even the less distinctly hydrophobic sols as substantive dyes and night-blue can be sensitized. Brossa[13] found that a coarse suspension of euglobulin can be peptized by these dyestuffs and that the clear sol so obtained is much more sensitive to electrolytes than the pure dyestuff sols. This fact is brought out in the following tables, not only for a negative Congo red sol but also for a positive one of night-blue.

TABLE V

Concentration of euglobulin 20 g. per liter; 10 cc. mixed with 20 cc. of Congo red solution. Concentration of Congo red solution 1 g. per liter. The Congo red solution used for comparison was made by mixing 10 cc. of water and 20 cc. of Congo red solution.

Concentration of NaCl, millimols per liter	Euglobulin-Congo red sol	Pure Congo red sol
5.0	Not flocculated, clear	Not flocculated, clear
12.5	Completely flocculated	Not flocculated, clear
25.0	Completely flocculated	Not flocculated, clear
50.0	Completely flocculated	Not flocculated, clear
100.0	Completely flocculated	Not flocculated, clear
200.0	Completely flocculated	Not flocculated, clear

TABLE VI

20 cc. euglobulin solution used in Table IV mixed with 20 cc. night-blue solution. Concentration 1 g. per liter. Pure night-blue sol used for comparison made by mixing 20 cc. of water and 20 cc. of sol.

Concentration of NaCl, millimols per liter	Mixed sols	Pure night-blue sol
12	Turbid	Not flocculated, clear
25	Completely flocculated	Not flocculated, clear
50	Completely flocculated	Completely flocculated
100	Completely flocculated	Completely flocculated
200	Not flocculated, clear*	Completely flocculated

* Due to peptization by high concentration of sodium chloride (see Tables I and III).

Recent work has shown that gelatin is able also to sensitize benzoin purple sols.[14]

The previous examples have indicated that gelatin belongs distinctly to the class of colloids capable of producing increased sensitivity. The same is true of casein. With albumin this action is not regularly observed. It does not sensitize the above-mentioned dyestuffs. Silver sol is not sensitized by gum arabic, saponin, or tannin. On the other hand, tannin is able to sensitize in a very distinct manner not only positive but also negative dye sols,[13] the theoretical importance of which fact will be developed later. For this reason, the experiments of the following tables were carried out with the negative alkali-blue sol as well as with that of the positive night-blue.

TABLE VII

Concentration of tannin sol 10 g. per liter; 1 cc. mixed with 10 cc. alkali-blue sol of a concentration of 1 g. per liter. Pure alkali-blue sol used for comparison made by mixing 10 cc. alkali-blue sol with 1 cc. of water.

Concentration of NaCl, millimols per liter	Mixed sol	Pure alkali-blue sol
50	Not flocculated, clear	
100	Not flocculated, clear	
250	Completely flocculated	
400	Completely flocculated	Not flocculated, clear
500	Completely flocculated	Not flocculated, clear
1,000	Completely flocculated	Completely flocculated
2,000	Completely flocculated	Completely flocculated

TABLE VIII

One and a half cubic centimeters of same tannin sol as used in Table VII mixed with 20 cc. of night-blue sol of a concentration of 0.5 g. per liter. Pure night-blue sol used for comparison made by mixing 1.5 cc. of water and 20 cc. night-blue sol.

Concentration of sodium sulfate, millimols per liter	Mixed sols	Pure night-blue sol
0.8	Not flocculated, clear	
2.0	Not flocculated, clear	
4.0	Completely flocculated	Not flocculated, clear
8.0	Completely flocculated	Not flocculated, clear
16.0	Completely flocculated	Completely flocculated

It is difficult to explain the important phenomena associated with the increase of sensitivity. In all probability it can be safely assumed that the two sols form a loose chemical combination. This is clearly indicated for the albumin ferric oxide sols.[5] It is also shown by the clear appearance of the flocculate from the sol containing albumin. Quantitative studies were made by mixing the same amount of albumin sol of known concentration

with different amounts of ferric oxide sol, coagulating with sodium chloride, and, after centrifuging, determining the albumin content by the Kjeldahl method. Table IX demonstrates that a considerable amount of albumin combined with the ferric oxide.

TABLE IX

Twenty-five cubic centimeters of albumin sol of a concentration of 8.04 g. per liter were mixed with 7.0 cc. of a ferric oxide sol containing 0.5, 1 2, 5, and 7 cc. of the original ferric oxide sol used in Table I. The mixed sols were coagulated by 5 cc. of a 0.1 normal solution of sodium chloride, and the albumin content of the solution determined after removing the flocculate by centrifuging.

Cc. of original ferric oxide sol used	Concentration of albumin in solution, grams per liter	Grams albumin adsorbed by 1 g. of ferric oxide
7.0	1.25	1.23
5.0	1.55	1.62
2.0	2.56	3.12
1.0	3.47	4.21
0.5	5.51	3.88

The amount of combined albumin increases at first in a linear manner with its concentration in the solution. At high concentrations a point of saturation is reached, a fairly constant maximum value. A similar behavior is exhibited by other substances of high molecular weight towards other adsorbents, as in the adsorption of the dyestuff, Ponceau R. R., by barium sulfate.[15] This is not an adsorption of the simplest type, as it is not reversible. The albumin cannot be separated from the ferric oxide by washing. It probably undergoes some chemical change on the surface of the ferric oxide, perhaps similar to that occurring in the process of denaturization.[16] It can scarcely be doubted that, in the increase of sensitivity produced by gelatin or metal sols or by tannin and euglobulin on dyestuff sols, a loose chemical combination of the different colloidal particles has occurred.

On cataphoresis the particles of the albumin ferric oxide sol travel much more slowly than those of the pure ferric oxide

sol.[5] According to Burton, the particles of the latter move 4 mm. in 5 minutes under an external potential of 220 volts, the electrodes being separated by 16.5 cm. The cataphoretic migration velocity μ was found to be 0.00106 cm. per second. For an albumin ferric oxide sol under identical conditions, the migration velocity was 1.5 mm. in 6 minutes, or μ equals 0.00042 cm. per second. μ is connected with the so-called electro-kinetic potential Σ, assumed to exist between the two sides of the electrical double layer of the particles by the equation

$$\Sigma = \frac{4\pi\eta\mu}{HD}$$

where η is the viscosity of the liquid, H the external potential in volts per centimeter, and D the dielectric constant. For the pure ferric oxide sol, Σ is equal to 12 millivolts, while for a sol containing albumin the value was 4.8 millivolts. In the same manner gelatin depresses the cataphoretic migration velocity of the particles of a Carey Lee silver sol (see Table X).

The above facts lead to the following conception of the increase in sensitivity. Solutions of gelatin, casein, and albumin are sols which may be assumed to contain the so-called colloidal ions in large amounts. The colloidal particles of these sols have comparatively small atomic weights, probably of the magnitude 10,000 to 100,000. These particles can be ionized and carry a correspondingly large number of charges. The total charge is large compared with that on a simple ion as K^+, but much smaller than the total charge carried by a gold particle in a gold sol, as the latter probably holds thousands of unit negative charges.

A correspondingly large number of cations from the solution form the opposite side of the electrical double layer. One can scarcely speak of a double layer, however, in connection with colloidal ions. The lines of force between oppositely charged ions run irregularly as with the ordinary electrolytic solution. They are not grouped around a certain middle point, as with the coarser particles of a gold sol. The characteristic behavior of such colloidal ions in soap solution has been studied by McBain.[17] Because of the amphoteric nature of protein solutions colloidal cations as well as colloidal anions are present, the former in acid solution, the latter in alkaline solution.

It can be safely assumed that, for the hydrophobe sols to which ferric oxide sol belongs by virtue of its reaction towards electrolytes, coagulation depends upon a reduction of the Σ potential of the particles accompanied by a decrease in their charge. Below a certain Σ value, particles coming in contact adhere to each other. The ion carrying a charge opposite to that of the micelle is responsible for the reduction of the Σ potential. It is probable that the colloidal ions can in some respects act like inorganic ions. They can reduce the Σ potential, lower the stability of hydrophobe sols, and even produce coagulation (see Table IV). Or they can bring the sol into a condition where the particles are partly discharged, when only a small concentration of electrolyte becomes necessary for coagulation.

In an approximately neutral albumin solution, only the presence of enough anions to discharge and sensitize the positive micelles of the ferric oxide sol need be assumed. In a gelatin solution enough cations must be assumed to be present to do the same for a negative silver sol or for an acid gold sol.

Completely in accord with this point of view is the fact that a gelatin solution does not sensitize a gold sol prepared by reduction with formaldehyde.[10] This sol is distinctly alkaline and the gelatin solution may not contain a sufficient number of cations.

Any increase in sensitivity produced by the cations can only appear when they are present in a low ratio to the micelle of the hydrophobe sol. When the particles of the hydrophobe are surrounded by larger amounts, they necessarily assume the properties of the hydrophile colloid. The protective action appears as soon as the concentration of hydrophile micelle is sufficiently large (see Table IV). The nature of the charge carried by the particles in this region is not definitely known. From Table IV, in the case of gelatin-silver sol, one would expect the particles to be positively charged, due to the discharge of negative silver particles by cations. The protective action would then be exerted by a layer of cations. But this is not the case. The gelatin-silver sol in the region of protective action is negatively charged[10] (see Table X).

This is understood after considering the amphoteric nature of the proteins. It appears possible that the gelatin micelles,

which cover the negative silver particles, lie with their positive end towards the silver particles while their negative end projects into the solution. The particles as a whole would then be negatively charged, which is observed to be the case. This conception has been developed from the theory of Langmuir[18] and Harkins.[19] According to this theory, the COOH group of the fatty acid is turned towards the water, leaving the hydrophobic end of the molecule to form the surface.

TABLE X

Concentration of gelatin, milligrams per liter	μ in centimeters per second	
0	−0.0016	
5	−0.0014	
10	−0.0009	
20	−0.0008	
30	−0.0007	flocculation begins
65	−0.0008	protected
70	−0.0011	protected
80	−0.0011	protected
100	−0.0011	protected
200	−0.0011	protected

While this conception of colloidal ions explains in a satisfactory manner the properties of albumin ferric oxide sol, gelatin-silver sol, etc., it may not be generally valid. It does not explain the increased sensitivity of dyestuff sols (both acid and basic) croduced by tannin (see Table X). Tannin is only slightly pissociated in solution, is not amphoteric, and can scarcely be donceived of as producing colloidal ions. On cataphoresis the migration velocity of the positive night-blue sol is probably reduced, while that of the negative alkali-blue sol is not appreciably changed. Nevertheless, both are sensitized to about the same extent (see Tables VII and VIII).

Tests were made to see if a change in hydrogen ion concentration due to the added tannin was responsible for the increased sensitivity. But tannin also increases the sensitivity of pure

hydrophile sols and renders them more easily coagulated by electrolytes. Kruyt[20] has explained its action on agar sols by assumptions based on the Langmuir-Harkins theory. The tannin molecule can be considered as polar. The glucose part of the molecule is pronouncedly hydrophilic, the digalloyl part is hydrophobic. It is probable that when the tannin particles come in contact with the agar micelles they become orientated so that the hydrophobic end projects into the solution. The new complex micelles are then as a whole hydrophobic the same as the tannin and agar micelles alone. This conception can also be employed for the tannin dyestuff sols. The dyestuff sols are certainly less hydrophobic than the metal or even the hydroxide sols. They are markedly more sensitive towards monovalent inorganic ions. It is conceivable that their micelles orientate themselves in a manner similar to that assumed for the agar micelle. The tannin dyestuff micelle as a whole would then be hydrophobic as are the tannin and dyestuff micelles alone.

Apparently the same conceptions that were forced upon us in the case of sensitization through tannin must be employed in the cases that were first explained from the point of view of colloidal ions, for example, the sensitization of dyestuff sols by euglobulin (see Tables VI and VII). Euglobulin, being a protein, is amphoteric and would be expected to sensitize positive as well as negative sols. But it is surprising to find that it exerts only a protective action on dyestuff sols and does not sensitize them. Furthermore, the influence of alkali is not that which we would expect from the action of colloidal ions on coagulation. It seems necessary to explain the behavior on other grounds than that of the amphoteric nature of the protein, and its ability to form two types of colloidal ions. There exists, perhaps, a polar orientation such as was assumed for tannin.

It is scarcely necessary to state that the explanation given for tannin represents only one of the possibilities. Some special form of chemical combination with the dyestuff is conceivable, or the factors influencing the increased sensitivity of hydrophobe sols by non-colloidal non-electrolytes may have to be considered. Sols may be sensitized by substances that are not colloids, as ferric oxide sol by camphor thymol, and other substances. It has been assumed hitherto that this is due to a change in the

dielectric constant at the boundary surface, which influenced the charge and therewith the stability of the particles.[21]

In any case, we have the following choice in dealing with this problem. If we desire a general solution, the influence of colloidal ions is certainly not sufficient, and it is necessary to test the hypothesis employed in the case of tannin to determine if it is generally valid. Or we may abandon the hope of a general solution and assume that the increased sensitivity is due to different factors in different cases. The conception of colloidal ions is completely satisfactory in many cases, but for others it is necessary to consider special possibilities, such as a polar structure in the case of tannin. It seems very probable that the phenomenon has no one special cause but must be referred to several factors.

Use of the Process

Although the above explanation of the increased sensitivity of sols leaves much to be desired, it is useful in the understanding of biological processes and in the solution of technical problems. Its usefulness depends upon the fact that the hydrophile colloids differ fundamentally in their ability to produce an increased sensitivity. These differences can be used as a means of identification. This is important because other convenient methods are often inadequate. This principle can be made use of in precipitating hydrophile colloids otherwise very difficult to separate from solution. The sol is mixed with a suitable hydrophobe sol, and the sensitized mixture precipitated by electrolytes.

The Recognition of Hydrophile Sols

By use of this process, Windisch and Bermann[22] could, with a high degree of probability, separate the colloids responsible for the essential properties of beer foam. The importance of colloids in the production of foam is well known, for filtration strongly reduces the ability of a solution to foam. It is necessary to distinguish between the colloids which produce foam and those whose chief function is to stabilize the foam. On filtering the wort through one of de Haen's membrane filters (No. 64) the filtrate still foams after vigorous shaking. This disappears,

however, in 70 to 80 seconds, while with unfiltered wort it persists for about 30 minutes. Part of the colloids left on the filter may be peptized by water. On adding this sol to the filtrate, the mixture recovers to a large degree its ability to produce a permanent froth. It is, therefore, the material retained on the filter and susceptible to peptization by water that imparts the comparative permanence to the foam.

It is desirable to determine the nature of these substances more closely. Chemically, they are not well characterized, but it happens that they differ markedly in their behavior towards ferric oxide sol. Windisch and Bermann named the concentration of sodium chloride necessary for coagulation of a given amount of ferric oxide sol, after adding a certain colloid, the iron number. This number alone suffices to characterize the hydrophile colloids if they are added to the same concentration of ferric oxide sol. This, however, was not possible, as the differences between the various colloids proved to be too large. A concentration of the hydrophile sol small enough to be suitable for gum arabic (a strongly sensitizing colloid) would render a weaker sensitizing colloid, as gelatin, inactive. A concentration large enough for gelatin was far too large for gum arabic. The gum arabic would be coagulated even without the addition of electrolyte. It is necessary, therefore, to use different concentrations of the hydrophile colloids. Windisch and Bermann discuss the iron number and the order of magnitude of the various colloids. Their data are given in Table XI.

TABLE XI

Hydrophile colloid	Order of magnitude	Iron number
Gum arabic	0.01	9.4
Agar	0.01	9.4
Gelatin	0.05	9.4
Witt's peptone	0.10	9.4
Albuminoses (from wort)	0.10	9.4
Barley gum	0.10	4.7
Dextrin	Acts only protectively	

Only the iron number and order of magnitude of the colloids (separated by the No. 64 ultra filter and then peptized) were determined. They found an order of magnitude of 0.1 and an iron number of 4.7, which correspond well with those of barley gum (Table XI). Barley gum, albuminoses, and peptins can be detected in the peptized colloids. A mixture of barley gum and Witt's peptone gave similar values. As it has been shown that the albuminoses are probably, above all colloids, responsible for the existence of the foam, we may conclude that barley gum produces the permanence of the foam

Stimulated by this research, Reitstötter[23] studied the iron number of different protein fractions of normal and pathological blood serums. For purification and separation of the different fractions, he used the above-described electrolytic method. On electrolyzing the serum in the middle chamber of the apparatus, the euglobulins separate out after the action has progressed sufficiently. These are then centrifuged off and a solution of albumins and paraglobulins obtained. By "paraglobulins" is meant the protein fractions lying between albumins and euglobulins. They remain behind on dissolving the albumins in pure water. They can be salted out in the same manner as euglobulins by half saturation of the solution with ammonium sulfate. Paraglobulins and albumins are, therefore, separated by half saturation of the solution with ammonium sulfate and filtering off the paraglobulins. The filtered material is then peptized by water and purified from salts by the electrolytic process previously described.

Reitstötter tested solutions of albumin and paraglobulin prepared in this manner for their action on ferric oxide sol. The determination of the iron number was sufficient for identification, since the differences between the protein fractions were not large enough to necessitate a determination of the concentration order. The measurements were made in exactly the same manner as those of Freundlich and Brossa.[1, 2, 3, 5] Not over 2 cc. of a 0.649 per cent ferric oxide sol were added to 25 cc. of a protein solution of about 0.6 per cent concentration. After adding 5 cc. of the mixture to 1 cc. of electrolyte solution the coagulation was measured.

TABLE XII

Protein hydrosol	Coagulation value in millimols per liter			
	Sodium chloride	Barium chloride	Sodium salicylate	Potassium sulfate
Protein-free ferric oxide sol	37.500	37.500	2.300	2.300
Albumins from human blood serum	0.290	0.290	0.097	0.097
Cattle albumins	0.235	0.235	0.097	0.097
Horse albumins	0.235	0.235	0.097	0.097
Diphtheria albumins	0.235	0.235	0.097	0.097
Paraglobulins from human blood serum	4.690	4.690	1.170	1.170
Cattle paraglobulins	4.690	4.690	1.170	1.170
Horse paraglobulins	4.690	4.690	1.170	1.170
Dysentery paraglobulins	2.340	2.350	0.586	0.290
Diphtheria paraglobulins	2.340	2.350	0.586	0.290
Tetanus paraglobulins	1.170	2.350	0.097	0.097
Chicken cholera paraglobulins	9.370	4.690	2.350	1.170
Hog erysipelas paraglobulins	4.690	4.690	1.170	1.170

Although the albumins of healthy and pathological serum reacted the same, the paraglobulins were in some cases distinctly different. The paraglobulins of dysentery, diphtheria, and tetanus sensitized much more strongly than those from normal serum; the chicken cholera paraglobulins sensitized more weakly. The paraglobulins of hog erysipelas reacted like those from normal serum. This is probably the first time that it has been possible to identify in a test tube, by means of colloid chemistry, the proteins of normal and pathological serum. This becomes important, since it has been shown that the gold number cannot be used as a means of differentiation.[24] The albumins do not exert so strong a protective action as the paraglobulins. However, the values for the albumins and paraglobulins lie too close together to serve as a characteristic means of identification.

Reitstötter did not study euglobulin in this manner. The usual methods could not be employed, as this protein precipitates in pure water. It must be taken up by a salt solution whose

concentration alone is great enough to coagulate the ferric oxide sol. Brossa[13] overcame this difficulty by using dyestuff sols in place of ferric oxide sols. It has already been stated that such sols are capable of peptizing coarse suspensions of euglobulin. The sol so obtained is strongly sensitized. A comparison between the euglobulins from different serums has not yet been made but, as was briefly mentioned above, a striking difference has been demonstrated between albumins and euglobulins, since the former exerts a protective action and the latter renders the sol more sensitive. Even in very low concentration, the albumins do not sensitize. Table XIII shows that albumins protect not only Congo red sols but also euglobulin Congo red sols.

TABLE XIII

Concentration of euglobulin suspension 40 g. per liter; 50 cc. mixed with 50 cc. of Congo red solution containing 1 g. per liter. The albumin solution was prepared by electrolysis and contained 10 g. per liter.

Cc. albumin solution added	Cc. water added	Effect on mixed sols
	1.0	Completely flocculated
0.1	0.9	Completely flocculated
0.2	0.8	Completely flocculated
0.4	0.6	Clear, not flocculated
1.0		Clear, not flocculated

In this research 1 cc. of albumin solution of different concentrations was added to 1 cc. of the mixed sols, and 0.5 cc. of normal sodium chloride solution added.

We may conclude that, in general, or at least towards dyestuff sols, euglobulin and albumin sols react in an opposite manner. Brossa established this for a number of cases. If then, in a serum, the concentration of albumin or of euglobulin is artificially increased, the new serum reacts differently towards a dyestuff sol. In order to increase the content of euglobulin, some of the protein prepared as described above is dissolved in a so-called normal solution (a salt solution of the same composition as that of the salts in the serum) and then added to the serum. To increase the ratio of albumin to paraglobulin, use is made of the

solution obtained by coagulating the euglobulins by electrolytes. It has been shown that the serums of different animal species of nearly equal protein content, but having different ratios of euglobulin to albumin, sensitize Congo red more strongly the greater the amount of euglobulin present. The ratio of euglobulin to albumin in the following serums is:

Rabbit serum	1:2.50
Human serum	1:1.51
Horse serum	1:0.58

Thus, a mixture of Congo red and rabbit serum is only coagulated by a high concentration of electrolyte, while a mixture of horse serum and Congo red is affected at low concentrations. In many pathological conditions this ratio of euglobulin to albumin is decidedly changed.

For healthy rabbit serum the ratio varies from 1: 2.36 to 1: 3.59. It changes to 1: 1.52 for a typhus immune serum. The immune serum, accordingly, sensitizes Congo red much more than the normal. The same can be demonstrated for the serum of men in normal health and men sick with typhus.

This research has lead to a distinction between euglobulins and albumins which is, perhaps, of general significance. According to recent work of von R. Stern,[25] the mechanism of the Wassermann and Sachs-Georgi reactions exhibit similar relationships. He was able to point out that a positive reaction in syphilitic serum was connected with the euglobulin fraction and not with the albumin of paraglobulin fractions. When the proteins of the serum are separated from one another in the manner described above, only the euglobulin and not the paraglobulin or albumin fractions gave a positive reaction in the Wassermann and Sachs-Georgi tests. In contrast with the results given in Table XII, only the euglobulin and not the paraglobulin fraction of syphilitic serum is changed. To speak more accurately, we must distinguish two parts in the euglobulin fraction. Only that fraction is active which is obtained by a complete purification from electrolytes. The labile euglobulin obtained by the action of carbon dioxide or by dilution of the serum is inactive. The change in the syphilitic euglobulins cannot of course be shown by a changed sensitivity of the dyestuff sol. It is possible

that the dyestuff sols are not sufficiently sensitive, while the colloidal solutions of the extracted lipoids are. If in the Sachs-Georgi reaction the lipoids extracted from syphilitic serum or from syphilitic euglobulin are more easily coagulated by salts than those from healthy serum or euglobulin itself, then the reaction consists in nothing more than a sensitization. The Wassermann reaction is intimately connected with that of Sachs-Georgi. The greater ease of flocculation in the Sachs-Georgi reaction corresponds to a stronger adsorption capacity for the substances that produce the Wassermann reaction.

This idea becomes more plausible when we recall that, according to Stern, the syphilitic euglobulins can be replaced by a colloid such as tannin, which acts in a manner similar to that of euglobulin in increasing the sensitivity of dyestuff sols. On mixing a healthy or Wassermann negative serum with tannin, a positive Wassermann or Sachs-Georgi test is obtained. However, it is not necessary to add the tannin to the serum. The solution of the extracted lipoids is sensitized by tannin, and becomes more easily coagulated by electrolytes. It was distinctly indicated that the effect is due to the specific nature of tannin, and is not a hydrogen ion effect of the weakly acid tannin solution. In a buffer solution of pH 7.0 to 7.6 the same result was obtained. According to our theory, this result can be explained as follows: The syphilitic euglobulin is distinctly more polar than the normal euglobulin and thereby makes the mixture of extracted colloid and euglobulin a hydrophobe sol in the same manner as was described for tannin. It should be especially emphasized that no change of charge can be detected either in the syphilitic euglobulin or in the syphilitic serum. Therefore, no explanation based on colloidal ions can be valid.

The phenomenon of agglutination can be conceived of as probably due to an increased sensitivity. It consists essentially in an adsorption by the bacteria of agglutinating substances, produced by their life process. They are thus changed by agglutinating bacteria to suspensions which are more easily precipitated by electrolytes than the original bacterial suspensions. From what little is known of the nature of agglutinin, it seems probable that it is a hydrophile colloid. The original bacterial suspension cannot, of course, be classed as a hydrophobe. It is not sensitive

to the effects of the cations of alkali or alkaline earth metals, while the suspension of the agglutinating bacteria has a coagulation value corresponding to that of a hydrophobe sol. Moreover, a typical hydrophile suspension is changed to a hydrophobe by agglutination. But it is an unsolved problem as to whether a sol must be a hydrophobe in order to be sensitized. Perhaps one hydrophile can sensitize a second one by changing its micelle into hydrophobic micelle. The dyestuff sols which have been discussed are so little affected by alkali salts that they cannot be classed as true hydrophobes. Kruyt has shown that the markedly hydrophile agar sol is changed to a hydrophobe by tannin. If this increased sensitivity is due to the same cause previously assumed to explain the action of tannin (the adsorption of a polar colloid accompanied by an orientation of this colloid so that the hydrophobe group projects into the solution), then it is possible that the same effect is produced by the adsorption of polar colloids by hydrophile micelle. There would then be no hesitation over classifying the behavior of tannin agar sols together with the agglutinating bacteria as a sensitization effect.

It is to be noted that agglutination is distinctly specific. Typhus bacteria, for example, are affected only by an agglutinin produced by inoculating an animal with typhus bacteria, and are not acted on by agglutinins obtained from other organisms. One recalls that according to Reitstötter's work, healthy and pathological paraglobulins, which in other respects are chemically and physically identical, can be distinguished through their different sensitization effects. It may be that sensitization is in many cases extremely delicate, and that slight differences may strongly depress the ability of colloids to sensitize. This leads apparently to the decided specificity of agglutination. Possibly bacteria and agglutinins must be adjusted to each other in a definite manner. Only then will the hydrophile groups of the agglutinin be oriented towards the solution and an increase in sensitivity be observed. If this adjustment does not occur at all, or is only imperfect, then no sensitization takes place.

The Removal of Proteins

The so-called deproteinization by ferric oxide sol, which was introduced by Michaelis and Rona,[26] depends upon sensitization.

A frequent problem in physiological work is that of removing protein from a liquid and at the same time changing the liquid as little as possible. In order to deproteinize serum, only 50 cc., diluted 12 to 14 times, is added drop by drop with constant shaking to 40 cc. of an electrolyte-free ferric oxide sol of suitable concentration. The amount of ferric oxide sol used can be adjusted so that the flocculate contains all the protein as well as all the iron. The filtrate is completely free from both. Since an amphoteric protein sensitizes positive as well as negative sols, it would seem possible to use a mastic sol in place of the ferric oxide sol. But this requires an addition of electrolyte for complete coagulation.

The removal of protein depends upon the same causes that are active in sensitization. The complex of ferric oxide and albumin micelle is coagulated by the salts present in the serum. But sensitization differs in one not unimportant respect from deproteinization. In sensitization the substances are mixed in the following order: (albumin sol + ferric oxide sol) + electrolyte solution. For the process of deproteinization the order is: (albumin sol + electrolyte) + ferric oxide sol.

In sensitization a mixed sol is prepared which is as free from electrolyte as possible. In deproteinization the mixed sol used in sensitization is of a decidedly amicronic nature. On addition of electrolyte it becomes gradually turbid and only precipitates after some hours. But in deproteinization, the flocculate separates quantitatively after some minutes. This is because the electrolyte present prevents the formation of amicronic particles. Consequently, large particles form rapidly and are soon coagulated. Contact probably plays a part here. According to Smoluchowski, contact is of great importance in accelerating coagulation when the colloidal particles exceed a certain size. In deproteinization the conditions are favorable for this contact influence. In sensitization they are unfavorable. The amounts of protein adsorbed in the two cases are not essentially different, as can be seen from Table IX.

Conclusions

Sensitization is experimentally a well-defined phenomenon of frequent occurrence. It consists in the action of a hydrophile

sol on a hydrophobe (perhaps on a second hydrophile sol), as a result of which the sol becomes more easily affected by electrolytes. It is improbable that any single explanation suffices to account for this behavior. At least, it cannot always be considered as due to the discharge of the micelles of a hydrophobe sol by colloidal ions. Thus the action of non-amphoteric tannin in sensitizing both positive and negative dyestuff sols and the occasional distinct differences in the ability of albumin and euglobulin to sensitize are difficult to explain on the hypothesis of colloidal ions. Apparently, it is necessary to take into account the polar nature of the sensitizing colloids, which enables them to orientate themselves so that the complex micelles have a more pronounced hydrophobic nature than those of the original hydrophobe sol. Sensitization is of general importance as a method of identifying hydrophile sols. It might be a profitable procedure to make use of sensitization methods in all problems where it is necessary to identify hydrophile sols.

REFERENCES

1. Zsigmondy: "Kolloidchemie," 3rd. ed., 1920, p. 149.
2. Henri, Lalou, Meyer and Stoel: *Compt. rend.*, **55** (1903), 1671.
3. Neisser and Friedemann: *Münch. med. Wochschr.*, **51** (1903), No. 11.
4. Pauli and Flecker: *Biochem Z.*, **41** (1912), 470.
5. Brossa and Freundlich: *Z. physik. Chem.*, **89** (1915), 306.
6. For an account of the coagulation of hydrophobe sols, see Freundlich, "Kapillarchemie," 2nd ed., 1920, p. 569.
7. Ruppel: *Ber. pharm. Ges.*, **30** (1920), 314; Reitstötter and Oester: *Chem. Ztg.* (1922), No. 5.
8. Bethe and Toropoff: *Z. physik. Chem.*, **88** (1914), 688; **89** (1915), 597.
9. Chick: *Biochem, Z.*, **7** (1913), 318.
10. Freundlich and Loening: *Kolloidchem. Beihefte*, **16** (1922), 1.
11. Donau: *Monatshefte*, **26** (1905), 525.
12. Ganz: *Kolloidchem. Beihefte*, **8** (1915), 251.
13. Brossa: *Kolloid Z.*, **32** (1923), 107.
14. Freundlich, Schuster, and Zocher: *Z. physik. Chem.*, **75** (1911), 710.
15. Mare: *Z. physik. Chem.*, **81** (1913), 641.
16. Biltz: *Biochem Z.*, **23** (1909), 27.
17. For a collected account of the researches of McBain and his co-workers, see Freundlich, "Kapillarchemie," 2nd ed., 1922, p. 774. *Cf.* Chap. XVI.
18. Langmuir: *J. Am. Chem. Soc.*, **38** (1916), 2221; **39** (1917), 1848.

19. Harkins, Brown, and Davies: *J. Am. Chem. Soc.*, **39** (1917), 354. Harkins, Davies and Clark: *ibid.*, **39** (1917), 541. Harkins, Clark, and Roberts: *ibid.*, **42** (1920), 700. *Cf.* Chap. VI.
20. Kruyt: *Kolloid Z.*, **31** (1922), 338.
21. Freundlich and Rona: *Biochem Z.*, **81** (1917), 87.
22. Windisch and Bermann: *Wochschr. für Brauerei*, **37** (1920), 130.
23. Reitstötter: *Z. Immunität*, **30** (1920), 507.
24. Reitstötter: *Ibid.*, **30** (1920), 486.
25. Stern, R.: *Klinische Wochenschrift*, **2** (1923), 145, and a later number yet to be published.
26. Michaelis and Rona: *Biochem Z.*, **2** (1907), 219; **3** (1907), 109; **4** (1907), 11; **5** (1907), 525; **7** (1908), 329; **8** (1908), 356; **14** (1908), 476. Rona and Oppler: *Ibid.*, **13** (1908), 121.
27. v. Smoluchowski: *Z. physik. Chem.*, **92** (1917), 155.

CHAPTER XIII

MUTUAL REACTIONS OF COLLOIDS

By

Arthur W. Thomas

When colloidal solutions are mixed, decrease in stability leading to precipitation may result, or, if one of the components of the mixture is a very stable colloid (hydrophilic) and is added in excess, while the other is rather unstable (hydrophobic), no visible change may take place and the solution will be found to show the stability and properties of the hydrophilic colloid.

The latter phenomenon is called "protective action." The former case, mutual precipitation of colloids, will be considered first.

Mutual Precipitation

The phenomenon of mutual precipitation of certain colloids was noted by Thomas Graham.[1] Linder and Picton[2] showed that mutually precipitating sols migrated oppositely in an electrical field. This was confirmed by Lottermoser,[3] who tried also to analyze the mixed gels resulting from mutual precipitation, but found quantitative results impossible of attainment, due to adsorption, etc. It was concluded then that oppositely charged sols precipitate each other. Bechhold,[4] Neisser and Friedman,[5] Henri[6] and his co-workers, and Teague and Buxton[7] published

[1] *J. Chem. Soc.*, **15** (1862), 246.

[2] *J. Chem. Soc.*, **71** (1897), 586.

[3] "Anorganische Kolloide," Stuttgart, 1901, p. 77 (through Zsigmondy-Spear: "Chemistry of Colloids," John Wiley & Sons, New York, 1917, p. 56.

[4] *Z. physik. Chem.*, **48** (1904), 385.

[5] *Münch. Med. Wochschr.*, **51** (1904), 465, 827.

[6] *Compt. rend. soc. biol.*, **55** (1903), 1666.

[7] *Z. physik. Chem.*, **60** (1907), 489.

work confirming this rule. Spring[8] stated that upon mixing aniline blue (which migrates to the anode) and Magdala red (which migrates to the cathode), no precipitation occurred, which he thought disproved the work of Linder and Picton and Lottermoser. Biltz[9] made a quantitative study of mutual precipitation by mixing measured quantities of sols which had been previously analyzed for the dispersed phases.

The following table is typical of the many combinations which he reported:

TABLE I

2 cc. sol containing, grams Sb_2S_3	13 cc. sol containing, grams Fe_2O_3	Appearance	
		Immediately	After 1 hour
5.6	20.8	Turbid	Slight precipitation
5.6	12.8	Turbid	Slight precipitation
5.6	8.0	Slow settling	Complete precipitation
5.6	6.4	Complete precipitation	Complete precipitation
5.6	4.8	Incomplete precipitation	Incomplete precipitation
5.6	3.2	Slight precipitation	Unchanged
5.6	0.8	Slight precipitation	Unchanged

The ratio between precipitating sols varied so much that the only conclusions to be drawn were that there are certain proportions in which sols must be mixed for complete precipitation; outside of this range there is partial precipitation within certain limits, and, if either sol is present in great excess, no precipitation occurs. Spring's failure to obtain precipitation with the dyes of opposite migration in an electrical field was due probably, to the proportions in which they were mixed, or to the fact that they do not react to form an insoluble compound.

In a comparison of precipitating values of the same sol against other sols, Biltz demonstrated that, while the optimum amount of a positive sol required to precipitate negative sols varies, the order is always the same, as shown below:

[8] *Bulletin de l'Acad. Roy. de Belg.* (Sciences) (1900), p. 483.

[9] *Ber.*, **37** (1904), 1095.

TABLE II

Milligrams of negative sol		Milligrams of positive sol					
		Fe_2O_3	ThO_2	CeO_2	ZrO_2	Cr_2O_3	Al_2O_3
Au	14	3	2.5	4	1.6	0.3	0.1–0.2
As_2S_3	24	13	6.0	4	2.0	0.5	2.0
Sb_2S_3	32	32	20.0	11	6.5	3.0	2.0

It was thus obvious that an equivalence between the optimum amounts of sols for precipitation exists, but not an equivalence between the particles of the dispersed phases of the sols. Billitzer[10] suggested that the equivalence is electrical, since at maximum precipitation there is no migration in an electrical field, and on either side the migration is in the direction of the sol in excess. He thought the equivalence would not be exact because of variations in the size and numbers of particles and in the concentration of the sols.

The following table is typical of his results:

TABLE III.—ARSENIOUS SULFIDE SOL MIXED WITH FERRIC OXIDE SOL
The As_2S_3 sol contained 2.07 mg. As_2S_3 per cubic centimeter, and the Fe_2O_3 sol, 3.036 mg. Fe_2O_3 per cubic centimeter

Cubic centimeters in 10 cc. of mixture		Appearance	Migration in electrical field of unprecipitated portion
Fe_2O_3 sol	As_2S_3 sol		
9.0	1.0	No change	To cathode
8.0	2.0	Slight turbidity	To cathode
7.0	3.0	Immediate turbidity, then precipitation	To cathode
5.0	5.0	Immediate precipitation	To cathode
3.0	7.0	Nearly complete precipitation	
2.0	8.0	Immediate precipitation	To anode
1.0	9.0	Immediate precipitation	To anode
0.2	9.8	Turbidity	To anode
10 cc. of 20 times diluted solution	10	Clear	To anode

[10] *Z. physik. Chem.*, **51** (1905), 129.

Billitzer also noted that when two colloids of like charge are mixed, the less stable one becomes more stable, assuming the properties of the more stable sol.

It is noted that, in the presence of a very large excess of one sol, no change in appearance of the system takes place. The lack of precipitation in such cases is ascribed to the fact that, while a neutralization of charges takes place, flocculation of the particles does not ensue, due to the fact that they are adsorbed or protected by the colloid in excess. That mixture which results in complete precipitation is frequently called the "isoelectric" mixture, since there is no migration in an electrical field after such an instance, for the obvious reason that nothing is left in suspension.

The theory of mutual precipitation, which arose from the foregoing experiments and from the opinion held by some that colloid stability resides in the mutual repulsion of like-charged particles, is that when oppositely charged colloidal particles are brought together an electrical neutralization ensues resulting in agglomeration of the particles; there being no electrical repulsive forces left, the particles must settle out of solution.

In 1910, Lottermoser[11] suggested that the equivalence may be that of the small amounts of stabilizing electrolyte in the sol, and that the precipitation may be due to a chemical reaction between the peptizing agents, by which they are removed. To test this he mixed positive silver iodide sols stabilized by silver nitrate and negative silver iodide sols stabilized by potassium iodide. The results summarized in Table IV indicate that the explanation holds for this precipitation at least. The quantities given are millimols at maximum precipitation.

These experiments, which point to a simple chemical reaction between the stabilizing electrolytes of the colloidal complexes in precipitation, have not attracted any attention.

Freundlich and Nathansohn[12] have recently shown that the mixing of pairs of certain like-charged colloids may result in mutual precipitation. For example, they found that arsenic trisulfide hydrosol precipitates Odén's sulfur hydrosol, both of

[11] *Kolloid-Z.*, **6** (1910), 78.
[12] *Kolloid-Z.*, **28** (1920), 258; **29** (1921), 16.

which migrate to the anode in an electrical field. Obviously, the electrical charge neutralization theory fails in this instance. Since Odén's sulfur sol contains pentathionic acid as stabilizing

Table IV

	Positive sol		Negative sol	
	AgI	$AgNO_3$	KI	AgI
1	0.210	0.052	0.055	0.220
2	0.220	0.055	0.050	0.200
3	0.225	0.009	0.010	0.245
4	0.245	0.010	0.017	0.180
5	0.270	0.009	0.010	0.040
6	0.240	0.010	0.007	0.033
7	0.038	0.007	0.010	0.240
8	0.040	0.010	0.008	0.196
9	0.115	0.010	0.010	0.240
10	0.115	0.010	0.007	0.170
11	0.225	0.009	0.010	0.115
12	0.240	0.010	0.008	0.088

agent (or as one of its stabilizing agents) and arsenious sulfide sol is stabilized by hydrogen sulfide, it was deduced that the mutual precipitation of these sols is a result of the following chemical reaction between their stabilizing agents:

$$5\ H_2S + H_2S_5O_6 \rightarrow 10S + 6H_2O$$

It was shown further by these investigators that the following combinations of negatively charged hydrosols result in coagulation: Odén's sulfur and Carey Lea's silver; von Weimarn's sulfur (made by pouring an alcoholic solution of sulfur into water) and Carey Lea's silver; Odén's sulfur and Kruyt's selenium. When Carey Lea's silver sol is mixed with arsenious sulfide hydrosol the mixture turns brown, and, if left in the dark, no further change takes place. Upon exposure to light, however, it undergoes a rapid change to olive green → emerald green → orange yellow (still clear), and then becomes turbid. The mechanism of this phenomenon is not understood.

Recently a careful quantitative study of mutual precipitation of ferric oxide hydrosol by silica hydrosol has been reported by Thomas and Johnson.[13] This paper offers strong evidence to the effect that mutual precipitation of certain hydrosols is the result of chemical reaction between the ions of the respective stabilizing electrolytes present, to which, in accordance with the "Complex Theory" of colloids, certain colloids owe their stability or solution-attractive forces.

To prove this point they were obliged to select sols which could be analyzed for the content of stabilizing agent. Instead of reporting merely the amounts of the insoluble part of the dispersed phases, as was customary formerly (and really of little or no significance), the amounts of stabilizing electrolytes are given by them.

The preparation and composition of the sols used are given in Tables V and VI.

TABLE V.—COMPOSITION OF FERRIC OXIDE SOLS

No.	Mols $FeCl_3$	Mols Fe_2O_3	$Fe_2O_3/FeCl_3$
1	0.00895	0.0482	5.35/1
2	0.01075	0.0509	4.8/1
3	0.00889	0.0483	5.37/1
4	0.00338	0.0294	8.65/1
6	0.00178	0.0191	10.6/1
15	0.00518	0.0507	9.8/1
17	0.00267	0.0346	13.0/1
20	0.00145	0.0267	18.5/1
21	0.00230	0.0367	15.9/1
23	0.00238	0.0339	14.3/1

Silicic acid sols were prepared by dissolving water glass (d., 1.4) in 10 times its weight of water and partially neutralizing to various degrees with hydrochloric acid. The sodium chloride formed was not removed because (1) the freshly prepared sols diffused quite readily through unglazed porcelain dialyzers and

[13] *J. Am. Chem. Soc.*, **45** (1923), 2532; Colloid Symposium Monograph, Univ. of Wisconsin, 1923, p. 187.

through ordinary collodion sacks; these sols after standing showed aggregation of particles (became opalescent) and then would not diffuse through the septa mentioned; but removal of sodium chloride by dialysis would also remove sodium hydroxide formed by hydrolysis of sodium silicate, which was not desired; (2) the presence of the sodium chloride did not complicate the results, as shown later.

TABLE VI.—COMPOSITION OF SILICIC ACID SOLS
In mols per liter

No.	1	2	3	4	5
SiO_2	0.221	0.208	0.305	0.437	0.186
NaOH	0.0327	0.0356	0.0294	0.135	0.0115
SiO_2: NaOH	6.7/1	5.8/1	10.4/1	3.5/1	1.6/1
NaCl	0.091	0.081	0.142	0.111	0.093

Various amounts of one sol were run from a burette into hard glass bacteriological tubes of uniform diameter and clearness and about 20 cc. in volume. Equal volumes of the other sol were run from a pipette or burette into the tube as quickly and as quietly as possible, to avoid mixing. The tubes were inverted two or three times with as little agitation as possible, to insure complete mixing of the sols. This was sufficient if the tubes were not more than three-fourths full and were revolved as they were inverted. The point of maximum precipitation could be clearly seen by successive stages; first, the greatest cloudiness in the series, followed by the first separation of particles, and usually the first sediment. The last was frequently over a wider range than the first two stages as the precipitating zone widened rapidly. All observations were made immediately after mixing by holding the series of tubes against a clean or open window. Artificial light was found to be quite unsatisfactory, as was the light late in the afternoon or on a dark day.

Some series precipitated more easily than others, probably because of greater agitation. Vigorous shaking usually precipitated the whole series immediately. A tube of greater diameter

than the others or of cloudy or marked glass appeared more cloudy and, consequently, was misleading. A few series were centrifuged, but the time required in placing them in the centrifuge and the force to throw out the fine particles resulted in complete precipitation over a wide range.

To avoid errors due to an unclean tube or some other factor, three or four determinations were made in each instance.

The effect of dilution of the sols is given in Table VII.

TABLE VII.—EFFECT OF DILUTION UPON MUTUAL PRECIPITATION

	Cc. Fe_2O_3 sol No. 6	Cc. SiO_2 No. 1	Precipitation results	Millimols HCl*	Millimols NaOH*
1.	1:0	1:10			
	5.3	1 to 10	All coagulated to solid		
2.	1:10	1:50			
	5.3	3.0	Partial	0.00284	0.00268
	5.3	3.5	Almost complete		
	5.3	4.1	Complete		
	5.3	4.5	Almost complete		
3.	1:50	1:250			
	5.3	4.5	Partial	0.00057	0.00064
	5.3	4.8 } 4.9	Complete		
	5.3	5.1 }	Complete		
	5.3	5.4	Partial		
4.	1:100	1:250			
	10	4.7	Much slower	0.00065	0.00053
	10	5.0	First to precipitate		
	10	5.3	Much slower		
	10	5.6	Much slower		

* The figures under the headings "HCl" and "NaOH" in the table express the amounts of ferric chloride and sodium silicate in terms of their hydrolysis products, HCl and NaOH, present in the respective sols in the mixture which resulted in first or complete precipitation.

This table shows that the dilution of mutually precipitating sols narrows and sharpens the zone of maximum precipitation, and that the variation in ratio between the sols varies no more than in successive experiments with the same dilution. If carried

beyond certain dilutions, coagulation is almost imperceptible or is so slow that it is very difficult to determine. The dilutions used for the work were the greatest giving sharp precipitations. Very unstable sols show considerably different ratios with dilution. This will be discussed later.

To avoid possible differences due to order of mixing, the order was always reversed at least once.

Table VIII gives the data found in determining the points of maximum precipitation in cases typical of 37 experiments made, and Table IX shows results obtained with one silica sol and several ferric oxide sols, which are typical of two other similar series.

TABLE VIIIA.—MUTUAL PRECIPITATION OF SILICIC ACID HYDROSOL NO. 1 WITH FERRIC OXIDE HYDROSOL NO. 20

Dilutions: Fe_2O_3 sol = 1:25 SiO_2 sol = 1:200

5.3 cc. of ferric oxide sol added to silicic acid sol

First test		Second test	
Cc. SiO_2 sol	Results	Cc. SiO_2 sol	Results
4.0	Partial precipitation	4.5	Partial later precipitation
5.0	First and heaviest precipitate	5.0	First to precipitate
6.0	Partial precipitation	5.5	
7.0	Only slightly cloudy	6.0	Partial later precipitation

It was evident that 5.2 cc. of silicic acid sol with 5.3 cc. of ferric oxide sol give the maximum precipitation.

TABLE VIIIB

Silicic acid sol added to 5.3 cc. of ferric oxide

Cc. SiO_2 sol	Results	Cc. SiO_2 sol	Results
4.8	Fourth to precipitate	5.4	Second to precipitate
5.0	Second to precipitate	5.6	Third to precipitate
5.2	First to precipitate		

Maximum precipitation is obtained with 5.2 cc. of silicic acid sol and 5.3 cc. of ferric oxide sol.

TABLE IX.—THE RATIO AT MAXIMUM PRECIPITATION OF SILICIC ACID SOL NO. 1 TO DIFFERENT FERRIC OXIDE SOLS

No.	Fe_2O_3 sol		Milli-equivalents		SiO_2 sol	
	Dilution	Cc.	Chloride	Sodium	Cc.	Dilution
1	1:100	10.0	0.00199	0.00151	4.6	1:100
2	1:100	5.3	0.00171	0.00124	3.8	1:100
3	1:100	10.0	0.00267	0.00180	5.5	1:100
4	1:100	10.0	0.00102	0.00112	3.5	1:100
6	1:100	10.0	0.00054	0.00065	5.0	1:250
15	1:50	5.3	0.00165	0.00155	9.5	1:200
17	1:50	5.3	0.00085	0.00085	5.2	1:200
20	1:25	5.3	0.00085	0.00085	5.2	1:200
21	1:25	5.3	0.00147	0.00164	10.0	1:200
23	1:25	5.3	0.00151	0.00155	9.5	1:200

Silicic acid sol No. 4 was precipitated at different dilutions against ferric oxide sols Nos. 4, 6, and 20. No clear zones could be determined, but in every case the milli-equivalents of sodium exceeded the milli-equivalents of chloride.

The precipitating volumes checked within 10 per cent in all cases except that of the very impure silicic acid sol No. 4.

To test the effect of the sodium chloride present upon the point of maximum precipitation, 0.03 g. of sodium chloride (an amount equal to 60 per cent of the amount of sodium chloride already present in the sol) was added to silicic acid sol No. 2 (diluted 1:200), and the sol precipitated with several ferric oxide sols.

The results showed that the sodium chloride is without influence on the mutual precipitation of silicic acid sols and ferric oxide sols, and, consequently, no error was introduced by its presence in the silicic acid sols used.

TABLE X.—THE RATIO OF FERRIC CHLORIDE EXPRESSED IN EQUIVALENTS OF HYDROCHLORIC ACID TO SODIUM SILICATE

Expressed in equivalents of sodium hydroxide in the 37 precipitations of ferric oxide sol and silicic acid cited in the foregoing tables. The values are milli-equivalents of sodium hydroxide per 0.001 milli-equivalents of hydrochloric acid.

The sols are arranged in the order of their purity, the ratio of sodium silicate in terms of sodium hydroxide to silicon dioxide decreasing from left to right, and the ratio of ferric chloride to ferric oxide decreasing from top to bottom.

		Silicic acid sols				
Number		4	2	1	3	5
Mols $NaOH/SiO_2$		1/3.5	1/5.8	1/6.7	1/10.4	1/16.1
Ferric oxide sols						
No.	Mols $FeCl_3/Fe_2O_3$					
2	1/ 4.8	.....	0.00061	0.00073	0.00080	
1	1/ 5.35	.....	0.00080	0.00055	0.00077	
3	1/ 5.37	.....	0.00073	0.00069	0.00077	
4	1/ 8.65	>100%	0.00096	0.00091	0.00090	
15	1/ 9.8	.....	0.00090	0.00100	0.00080	0.00029
6	1/10.6	>100%	0.00106	0.00094	0.00082	
17	1/13.0	.....	0.00101	0.00090	0.00080	0.00043
23	1/14.3	.....	0.00101	0.00091	0.00090	0.00048
21	1/15.9	>100%	0.00098	0.00110	0.00080	0.00044
20	1/18.5	.....	0.00093	0.00100	0.00080	
Av. (excl. of 2, 1, 3)		>100%	0.00098	0.00095	0.00083	0.00041

Table X shows that over a wide range of ratios between peptizing agent and dispersed phases of sols there is a constant ratio between the peptizing agents of mutually precipitating sols and a greatly varying ratio between the insoluble part of the dispersed phases. This leads to the conclusion that the precipitation is due to removal of the peptizing agents by a chemical action between them. As no definite formulas can be given for the silicates, it is impossible to express the reaction between sodium silicate and ferric chloride in an equation. However, the peptizing ferric chloride and sodium silicate can be given in terms of their hydrolysis

products which are in equilibrium with the dispersed phase complexes, and, consequently, in the mutual precipitation of ferric oxide and silicic acid sols the reaction may be expressed as $HCl + NaOH \rightarrow NaCl + H_2O$.

Another indication of such a reaction is given by the difference of hydrogen ion concentration in the supernatant liquid of precipitation of varying degrees. Various amounts of silicic acid sol No. 3 (diluted 1:25) were added to 25 cc. of ferric oxide sol No. 4 (diluted 1:10), the precipitates allowed to settle, and the hydrogen ion concentrations of the supernatant liquids determined with the results given in Table XI. The ferric oxide sol showed a Sörensen value (pH) of 5, while the silicic oxide sol was slightly alkaline to phenolphthalein.

TABLE XI.—CHANGE IN HYDROGEN ION CONCENTRATION WITH VARYING PRECIPITATION OF FERRIC OXIDE AND SILICIC ACID SOLS

Silicic acid sol, cc.	Remarks	pH
10	Very slight precipitation Excess of Fe_2O_3 sol	5.6
16	Maximum precipitation	6.8
18	Second of series to precipitate	7.8
20	Slow precipitation	Excess of SiO_2 sol > 8.3 (alkaline to phenolphthalein)

Thus it is evident that maximum precipitation occurs at neutrality as the chemical equivalence of the peptizing electrolyte demands and that the acidity increases with an excess of ferric oxide sol, and the alkalinity increases with an excess of silicic acid sol.

The ferric oxide sols, excluding Nos. 1, 2, and 3 (which contain the greatest amount of the peptizing agent in proportion to the dispersed phase), give a 1:1 ratio with silicic acid sols Nos. 1 and 2. With silicic acid sol No. 3, the same ferric oxide sols give a constant ratio with the ferric chloride of the same ferric oxide sols. As the sol becomes purer in respect to peptizing agent,

it becomes more unstable and the precipitating ratios become more inconstant. This agrees with the general experience with "pure" ferric oxide sols. It is known that when a certain degree of "purity" is exceeded in a sol, the sol precipitates. The sol containing only a little more than the necessary minimum of peptizing agent is in a metastable condition, and the least disturbance will precipitate it. This may easily account for the ready precipitation of the pure ferric oxide sols.

The effect of diluting unstable sols in mutual precipitation is shown in Table XII.

TABLE XII.—PRECIPITATION OF FERRIC OXIDE SOL NO. 17 WITH SILICIC ACID SOL NO. 5 OF VARIOUS DILUTIONS

Fe_2O_3 sol, 1:50	Milli-equivalents of HCl, 0.00160		
SiO_2 sol	1:50	1:100	1:200
NaOH milli-equivalents	0.00057	0.00069	0.00080
NaOH eq. of HCl eq. %	35.	43.	50.

Thus it is seen that the reaction between very "pure" sols tends to approach chemical equivalence upon dilution, which is to be expected, since the individual particles becoming widely separated upon dilution have less chance of aggregating and thus settling out. In the meantime there is more chance for a complete reaction between the peptizing agents.

Both ferric oxide and silicic acid sols show erratic results in precipitation, if they contain large amounts of peptizing agent. This is undoubtedly due to the fact that some of the unaffected peptizing agent is adsorbed in the coagulum and carried down with it.

Thomas and Johnson tried also to study the mutual precipitation of ferric oxide and arsenious sulfide sols as a function of the reaction between the stabilizing ferric chloride of the iron oxide sol and of the stabilizing hydrogen sulfide of the arsenious sulfide sol. The errors existing in the present quantitative methods for the determinations of arsenic and of sulfur are large enough to make an analysis of the $x As_2S_3.yH_2S$ complex impos-

sible, due to the small amounts involved. They reasoned that if, in the mutual precipitation of ferric oxide sol and arsenious sulfide sol, a chemical reaction takes place between the ferric chloride and hydrogen sulfide of peptization, one of the following reactions may take place: (1) $H_2S + 2FeCl_3 \rightarrow 2FeCl_2 + S + 2HCl$; (2) $3H_2S + 2FeCl_3 \rightarrow 2FeS + S + 6HCl$.

In most precipitations there is no evidence of the latter reaction, as the precipitate is yellow. When, however, the sol contains a large amount of hydrogen sulfide, a blackening develops which can be explained by the formation of ferrous sulfide.

To test the supposition that the mutual precipitation between ferric oxide sol and arsenious sulfide sol is due to the oxidation of the sulfide ion of the peptizing hydrogen sulfide by the ferric ion of the peptizing ferric chloride, the following experiment was performed.

Five hundred cubic centimeters of an arsenic trisulfide sol were precipitated with ferric oxide sol No. 4, the precipitate dried and extracted with carbon disulfide. *Sulfur was recovered.* Since arsenious sulfide sols are most likely to contain sulfur after exposure to air, a "blank" was run wherein an equal quantity of sol was precipitated by aluminum sulfate, the precipitate dried, extracted, and the sulfur found subtracted from that obtained in the main experiment.

The presence of sulfur in the gel (in excess of the small amount originally present in the sulfide sol) can be accounted for only through the following chemical reaction

$$S^{=} + 2Fe^{+++} \rightarrow S^{0} + 2Fe^{++}$$

In view of the evidence submitted by Freundlich and Nathansohn and by Thomas and Johnson, it would appear that the older electrical charge theory of colloid interaction must give way to the chemical reaction hypothesis.

The degree of dispersion of the interacting colloids has been claimed to be significant by Galecki and Katorski.[14] They state that the precipitating power of one colloid upon another increases with increasing degree of dispersion, and believe they have demonstrated this fact by the reaction of a ferric oxide

[14] *Kolloid-Z.*, **13** (1913), 43.

hydrosol with (1) a gold hydrosol made by the formaldehyde reduction method (Au_F), and (2) a gold hydrosol prepared by reduction with phosphorus (Au_P). Ultramicroscopic observations showed the Au_P sol to be of higher degree of dispersion than the Au_F. The ferric oxide sol which they used contained 10.28 mg. Fe_2O_3 per cubic centimeter.

1 mg. Au_F precipitated 4.98 mg. Fe_2O_3.
1 mg. Au_P precipitated 18.36 mg. Fe_2O_3.
When the ferric oxide sol was diluted three times,
1 mg. Au_F precipitated 4.65 mg. Fe_2O_3.
1 mg. Au_P precipitated 20.65 mg. Fe_2O_3.

At first glance their claim appears plausible, but when one considers that these gold sols are prepared from gold chloride, sodium carbonate, and varying amounts of formaldehyde or of phosphorus, resulting not only in reduction of the auric ion but in oxidation of the reducing agents, forming different amounts and kinds of products in each instance, it is evident that such a simple mechanical explanation is of doubtful value.

Hydrophilic colloids, such as the proteins, mutually precipitate under certain conditions. Kutscher[15] and Bang[16] showed that protamine precipitates other proteins. Malengreau[17] found that histone mutually precipitates with hemoglobin, serum albumin, and globulin.

The significance of the hydrogen ion concentration of the solution in the mutual precipitation of proteins was demonstrated by Michaelis and Davidsohn.[18] They stated that when two amphoteric colloids, such as proteins, are brought together in solution, a compound may be formed and precipitated, the condition for most complete precipitation being a hydrogen ion concentration between those of the isoelectric points of the reacting ampholytes. Thus, when one protein is present as a cation and the other as an anion, the formation of a compound is to be expected, whereas when both proteins are cations (the pH is acid to both of their isoelectric points), or where both are anions (the pH is on the

[15] *Z. physiol. Chem.*, **23** (1897), 117.
[16] *Ibid.*, **27** (1899), 483.
[17] *Le Cellule*, **21** (1903), 121.
[18] *Biochem. Z.*, **39** (1912), 496.

alkaline side of both isoelectric points), a combination between them is not to be expected. The combination between pairs of proteins has resulted in insoluble complexes in practically all cases tried, but, since a great deal of work has yet to be done on this subject, it is not safe, at present, to state that proteins always precipitate one another if mixed together at a pH between their isoelectric points. Michaelis and Davidsohn found also that the optimum pH for the mutual precipitation of proteins varies with the relative amounts of the proteins reacting; when a large excess of one component is present, the pH optimum for precipitation will shift toward the isoelectric point of this component.

The precipitation optimum for a mixture of aqueous dispersions of nucleic acid and serum albumin was found to be at pH 4.05 to 4.22, which is between the isoelectric points of the components, while a mixture of nucleic acid and heat-denatured serum albumin precipitated best at pH 3.8. When the ratio of nucleic acid to the albumin was increased, the optimum reaction for precipitation shifted toward the acid side, *i.e.*, toward the isoelectric point of nucleic acid.

Casein and nucleic acid precipitated each other in a pH range of 4.05 to 2.52, depending upon whether casein or nucleic acid was present in excess. Mixtures of casein with both genuine and denatured serum albumin were found to result in precipitation. Variation in the mass relationships made no difference, due to the fact that the isoelectric points of these proteins are so close together.

Beth af Ugglas[19] reported the mutual reactions between clupein, thymushistone, casein, and horse blood hemoglobin. The protamin precipitates hemoglobin, the coagulum being peptized by excess of hemoglobin and by acid. The coagula obtained always had the composition of 95 per cent hemoglobin and 5 per cent protamin. Histone acts like the protamin on hemoglobin, the coagulum consisting of one part histone to two parts of hemoglobin. In both cases the dissolution of the coagulum by acid was reversed upon addition of ammonia.

The precipitation of casein by protamin as shown by Hunter[20] was also studied by af Ugglas, who found that a "neutral"

[19] *Biochem. Z.*, **61** (1914), 469.

[20] *Z. physiol. Chem.*, **53** (1907), 526.

protamin precipitated a "neutral" caseinate. The coagulum is insoluble in cold water, but soluble in warm water and in saturated sodium chloride solution. It is also peptized by excess of casein. The composition of the coagulum was about 94 per cent casein and 6 per cent protamin. Histone was found to act upon casein just like the protamin; the precipitate dissolving in dilute alkali and in excess of casein. When dissolved in alkali and reprecipitated by acid, the coagulum showed no alteration in composition from the ratio of 71 per cent casein and 29 per cent histone.

Hemoglobin and casein were found not to react in slightly alkaline solution, but precipitated each other in "neutral" solution, the coagulum dissolving in dilute alkaline solution and reprecipitating upon acidification. Af Ugglas found the coagulum to be composed of two parts of hemoglobin to one of casein.

In the experiments reported by af Ugglas the significance of the hydrogen ion concentration of the solutions in the precipitations is evident, although unfortunately not measured by the investigator.

Based upon 16,700 as the molecular weight of hemoglobin, and the value of 8,888 for casein, as given by van Slyke and Bosworth,[21] the casein hemoglobin precipitate consisted of one molecule of casein to one of hemoglobin. Assuming 6,122 as the molecular weight of histone,[22] a ratio of two molecules of casein to one of histone would call for a composition of 26 per cent histone and 74 per cent casein. Analysis of the coagulum showed 29 and 71 per cent respectively.

Michaelis and Davidsohn[23] investigated the influence of pH in specific precipitations. Using as precipitin the serum of a rabbit that had been previously sensitized with sheep serum, flocculation of this precipitin and sheep serum was obtained equally as well at pH 9 as at pH 5, thus showing no dependence upon the hydrogen ion concentration. This sort of reaction is then different from protein mutual precipitation.

De Kruif and Northrup[24] have recently shown the same to be true for the agglutination of *Bacillus typhosus* by immune serum.

[21] *J. Biol. Chem.*, **14** (1913), 227.

[22] Bang, *Beitr. chem. Physiol. Path.*, **4** (1903), 348.

[23] *Biochem. Z.*, **47** (1912), 59.

[24] *J. Gen. Physiol.*, **5** (1922), 127.

They found that the amount of immune body combined with the organisms is constant from pH 9 to pH 3.7, and that the combination is not caused by a difference in sign of the charge carried by the immune body and the organism.

The flocculation of bacteria by proteins, however, has been found to be similar to protein mutual precipitations. Eggerth and Bellows[25] found that a suspension of *Bacterium coli* is agglutinated by gelatin, crystallized egg albumin, proteoses, edestin, and oxyhemoglobin at hydrogen ion concentrations between the isoelectric point of the protein and the acid flocculation zone of the bacterial suspensions, the latter having been found to lie between pH 1.6 and 3.0. The following table is typical of a series reported by these investigators.

TABLE XIII.—FLOCCULATION OF *B. Coli* SUSPENSION WITH EGG ALBUMIN

1.0 cc. buffer mixture + 0.5 cc. albumin solution + 0.5 cc. *B. coli* suspension

Concentration of albumin	Lactate buffers							
0	−	−	−	−	−	+	−	−
1:400,000	−	−	−	−	−	+	−	−
1:40,000	−	−	−	+	+	+	+	−
1:4,000	−	X	X	X	X	X	+	−
1:400	−	X	X	−	−	−	−	−
pH =	4.7	4.4	4.1	3.8	3.5	3.3	3.0	2.7

Temperature = 40°C. X = agglutination within 1 hour. + = agglutination within 4 hours.

A second strain of the organism was agglutinated at pH 4.7 by an albumin concentration of 1:150. It is seen that as the ratio of albumin to bacteria increases, the optimum flocculation point shifts toward the isoelectric point of the albumin.

The proteins of blood serum are precipitated by lecithin suspensions at hydrogen ion concentrations between the isoelectric points of the reacting substances. The isoelectric points

[25] *J. Gen. Physiol.*, **4** (1922), 669.

(or flocculation optima) of lecithins have been found to vary from pH 2 to 4, depending upon the source.[26] As the proportion of blood serum to lecithin is increased, the optimum precipitation tends to shift toward the reaction of the isoelectric point of the blood serum proteins.

Jarisch[27] also finds precipitation between lecithin and dialyzed blood serum. Soaps and colloidal suspensions of fatty acids also cause flocculation of a protein in dialyzed blood serum, but not in the presence of 0.012 N sodium chloride.

An interesting example of the mutual precipitation of hydrophilic or "protective" colloids is that of gelatin with gum arabic. Gum arabic appears to consist mainly of a complex carbohydrate acid combined with more or less calcium as a calcium salt. In view of the recent work of Jacques Loeb, one would expect a precipitation of gelatin by gum arabic in solutions on the acid side of pH 4.7 (the isoelectric point of gelatin), if gelatin "arabate" is an insoluble complex.

Thomas Graham (1861) showed that gelatin is precipitated by "gummic acid," the coagulum settling out to form a jelly-like mass. This reaction has been rediscovered by Tiebackx,[28] whose attention to it was aroused by the fact that oil-in-water emulsions "broke" upon mixing if one was emulsified with gum arabic and if gelatin was the emulsifying agent in the other. He found that gelatin and gum arabic mutually precipitate in a solution sufficiently acid to insure the presence of gelatin cations, the coagulum setting to a jelly when warmed. In the presence of an excess of gelatin this precipitation does not occur. This is an example of the "protective" effect of an excess of one component as seen in the mutual precipitation of inorganic colloids discussed earlier in this chapter, and will be referred to again later. Tiebackx noted that gum tragacanth precipitates gelatin. The flocculation of gelatin by gum arabic has been reported also by Luppo-Cramer.[29]

The precipitation of proteins by tannin may properly be included here, since it is generally agreed that tannin is more

[26] Feinschmidt: *Biochem. Z.*, **38** (1912), 244.
[27] *Klin. Wochschr.*, **1** (1922), 71 (through *Chem. Abs.*, **16** (1922), 2871).
[28] *Kolloid-Z.*, **8** (1911), 198, 238; **31** (1922), 102.
[29] *Phot. Korr.*, **51** (1913), 111.

colloidal than "crystalloidal" in nature. Tannin is a well-known protein precipitant, one being used as a test for the other. The precipitation of gelatin by tannin has been studied rather extensively, and, of course, the reaction between tannins and hide protein in leather manufacture, but, since the latter protein is insoluble, a discussion of its combination with tannin is outside the realm of this chapter.

The discovery of the gelatin-tannin coagulation is attributed to Seguin,[30] although Seymour-Jones[31] claims that, in 1762, Lewis found that galls contained an astringent substance capable of precipitating gelatin from solution. The reaction was studied from a quantitative point of view by Humphrey Davy.[32]

An investigation has been recently published by Thomas and Frieden.[33] They found that the optimum precipitation of gelatin and tannic acid, in the absence of salts, takes place at pH^+ 4.4 to 4.6. The effect of pH is shown in Table XIV. It is seen that maximum precipitation is obtained on the acid side of the

TABLE XIV

pH	Appearance of supernatant solution	Volume of precipitate, cubic centimeters
3.9	Clear, yellowish	0.90
4.1	Clear, yellowish	1.10
4.3	Clear, yellowish	1.15
4.5	Clear, yellowish	1.20
4.7	Cloudy	0.90
4.9	Milky	0.80
5.1	Opalescent	0
5.3	Slightly opalescent	0

isolectric point of the protein, an insoluble compound being formed through the interaction of gelatin cations and tannin anions. The optimum at a hydrogen ion concentration just

[30] *Ann. chim.*, **20** (1796), 15.
[31] *J. Soc. Leather Trades Chem.*, **4** (1920), 119.
[32] *Phil. Trans.*, **93** (1803), 233.
[33] *Ind. Eng. Chem.*, **15** (1923), 839.

slightly above that of the isoelectric point of the gelatin followed by a drop at higher acidities is explainable due to the fact that tannic acid is an exceedingly weak acid. A precipitation slightly on the alkaline side of the isoelectric point of protein is not unexpected, since the ionization of gelatin as a base has not vanished at pH 4.9. It must be borne in mind that a protein is ionized both as a base and an acid at its isoelectric point. The view that it is completely un-ionized at this point is wrong. It is ionized but its basic and acidic dissociations are equal in extent, and as the alkalinity (or acidity) is increased, its basic (or acidic) degree of dissociation decreases and its power to combine with acids (or bases) likewise decreases.

The influence of the relative proportions of gelatin and tannin are shown in Table XV, where the reaction was maintained at pH 4.

TABLE XV

Ratio of tannin to gelatin	Volume of precipitate, cubic centimeters	Appearance of supernatant liquid	Test of supernatant liquid for	
			Gelatin	Tannin
20	0.4	Clear, yellow	−	+
10	0.9	Clear, yellow	−	+
8	0.9	Clear, yellow	−	+
6	1.4	Clear, slight yellow	−	+
4	1.5	Clear, slight yellow	−	+
2	2.5	Clear, colorless	−	Almost −
1	1.8	Milky	+	

The best precipitation is obtained at a ratio of two parts tannin to one of gelatin. An excess of either results in "peptization," just as in the case of inorganic colloids. The importance of the correct ratio of gelatin to tannin is shown by the misstatement of Michaelis and Davidsohn[34] to the effect that the optimum pH varies from 3.8 to 5.7. This was due to the fact that, in a number of the few experiments tried by them, there was an excess of gelatin.

[34] *Biochem. Z.*, **54** (1914), 323.

Thomas and Frieden found that certain vegetable tannin extracts acted differently from pure tannic acid in respect to optimum hydrogen ion concentration. This is shown in Table XVI.

TABLE XVI.—OPTIMUM pH RANGE FOR TANNIN-GELATIN PRECIPITATION

Extract	pH
Larch	4.0 to 3.5*
Oak	3.5 to 4.0
Hemlock	4.0 to 4.5
Quebracho	4.0 to 4.5
Wattle	4.5 to 4.0
Gambier	3.5 to 4.0

* The optimum reaction is given last in each case.

An interesting comparison of the delicacy of the reaction between commercial tannins and gelatin at optimum pH and in distilled water with no pH control is exhibited in Table XVII.

TABLE XVII

Extract	Limit of detection at optimum pH *1 part in	In distilled water * 1 part in
Larch	150,000	20,000
Oak	150,000	7,500
Hemlock	130,000	6,500
Quebracho	130,000	17,000
Wattle	200,000	20,000
Gambier	110,000	30,000

* Parts tannin in parts water.

The significance of pH control is well illustrated in the table above. When the reaction is used as a test either for a protein or for tannin, the addition of sodium chloride will broaden the pH range of precipitation and thus counterbalance to an extent a lack of pH regulation, although it will not increase the sensitivity of the precipitation at the optimum pH.

Protective Action

When a solution of a hydrophilic colloid is added to a less stable colloidal dispersion, or suspension, generally there is no change in appearance of the system and the less stable dispersion is found to have become more stable, *i.e.*, it is no longer so sensitive toward coagulation by either the addition of electrolytes or by evaporation to dryness. The less stable dispersion is said to have been "protected" by the hydrophilic colloid; hence the term "protective colloid," which is commonly applied to the hydrophilic colloids, such as gelatin, gum arabic, albumin, etc.

The discovery of protective action may justly be attributed to Michael Faraday, who noted that the addition of gelatin to his colloidal gold dispersions rendered them so stable that it was possible to evaporate them to dryness without change in color.[35]

Since there appears to be a general tendency to regard "protective" colloids as a class that always confers increased stability upon lyophobic colloids, it would be well to stop for a moment in order to show that "protective" colloids do not differ so radically from others in their conduct in mutual reactions. It is more a difference in degree than in kind. For example, hydrophilic colloids may precipitate other dispersions. We have just reviewed a number of instances where certain protective colloids precipitate each other.

The precipitation of alumina hydrosol by gelatin was observed by Thomas Graham. This thoroughgoing scientist also describes the mutual precipitation of colloidal silica by gelatin.[36] It is interesting to note that he attempted to follow this reaction quantitatively as shown in the following quotation from his paper:

> Silicate of gelatin falls as a flaky, white, and opaque substance, when the solution of silicic acid is added gradually to a solution of gelatin in excess. The precipitate is insoluble in water and is not decomposed by washing. Silicate of gelatin prepared in the manner described contains 100 silicic acid to about 92 gelatin. In the humid state the gelatin of this compound does not putrefy. When a solution of gelatin was poured into silicic acid in excess, the cosilicate of gelatin formed gave, upon analysis, 100 silicic acid with 56 gelatin.

[35] *Phil. Trans.*, **147** (1857), 184.
[36] *J. Chem. Soc.*, **15** (1862), 246.

This appears to have been overlooked, since in recent colloid literature one notes reports of the discovery that sometimes protective colloids do not protect. One such report is that of Brossa and Freundlich.[37] These authors find that the addition of a small amount of well-dialyzed albumin solution to ferric oxide hydrosol renders the latter more sensitive toward the precipitating influence of electrolytes rather than more stable. The explanation for this is simple, and will be returned to later. It is evident that the findings of Graham were overlooked as well as the more recent papers of Friedmann[38] and of Pauli and Flecker.[39]

Friedmann noted that albumin, when used in the proper proportion, would precipitate hydrosols of Ag, As_2S_3, Sb_2S_3, SiO_2, MoO_2, Fe_2O_3, and Cr_2O_3. Pauli and Flecker carried out a large number of experiments on the coagulation of a series of inorganic colloids by serum proteins and gelatin.

Protective colloids may protect less stable dispersions or may render then still less stable, even resulting in mutual precipitation, depending upon the signs of the charges of the protector and hydrophobe, and upon the relative proportions of the two sols brought together. The significance of the signs of the charges carried by the two colloids interacting was shown by Billitzer.[10] He pointed out that a solution of gelatin which contains a trace of acid will precipitate arsenious sulfide sol, while, when a negative charge is conferred upon the gelatin by addition of a very small amount of ammonium hydroxide, it will then mutually precipitate with ferric oxide sol. If, however, a slightly positive gelatin is mixed with the ferric oxide sol, protection takes place. The complex is not precipitated by the addition of a slight amount of ammonium hydroxide, but the sign of the charge of the complex is changed from positive to negative.

In view of the modern chemistry of protein solutions, and the envelope theory of protection enunciated by Bechhold,[40] an explanation is available. When a gelatin solution is acidified with hydrochloric acid, for example, the gelatin combines with

[37] *Z. physik. Chem.*, **89** (1915), 306.
[38] *Archiv für Hygiene*, **55** (1906), 361.
[39] *Biochem. Z.*, **41** (1912), 461.
[40] *Z. physik. Chem.*, **48** (1904), 385.

the acid to form the salt, gelatin chloride, which is ionized into gelatin cations and chloride anions, *i.e.*, the gelatin particles are positively charged. Hence, when this sol is added to the negatively charged arsenious sulfide sol, we have a case similar to the mutual reaction of ferric oxide sol and antimony sulfide sol described early in this chapter. At or near the relative proportions of gelatin and arsenious sulfide sols, where the "charges exactly neutralize each other," there will be mutual precipitation. In the presence of a large excess of either the sulfide sol or of gelatin there will be no coagulation. Since gelatin is amphoteric, it shows a similar behavior toward ferric oxide hydrosol. Addition of ammonium hydroxide to a gelatin solution results in the formation of ammonium gelatinate. Consequently, there will be a range in relative proportions of gelatin (now negatively charged) and of ferric oxide sol where mutual precipitation will take place, and in the cases of a large excess of either iron oxide or of gelatin there will be no precipitation. Certain colloid chemists do not favor the idea of the formation of salts by gelatin, but they will admit that gelatin becomes positively charged in acid and negatively charged in alkaline solutions.

The writer has used the generally accepted language in discussing the mutual precipitation of gelatin with arsenious sulfide and with ferric oxide sols. He prefers the following which deals with the same as simple chemical reactions. The solution of gelatin in dilute ammonium hydroxide contains not only ammonium and gelatinate ions but also ammonium hydroxide and its ionization products, *e.g.*, ammonium gelatinate hydrolyzes in aqueous solution. The stability of ferric oxide sol is due to the ferric chloride, or acetate, as the case may be, that is combined with (or adsorbed by) the ferric oxide particles. When these two sols are mixed, the ammonium hydroxide and ferric chloride or acetate react to form hydrous ferric oxide. If the condition of "isoelectric" proportions of the interacting sols obtains, then precipitation ensues, due to the removal of all of the stabilizing or peptizing agent of the ferric oxide sol, and to the fact that there is not sufficient gelatin present to "protect" it, *i.e.*, to form envelopes around the ferric oxide particles and thus keep the latter in dispersion through the solution forces of the gelatin. It must be noted as well that gelatin, at or near its

isoelectric point (the hydrogen ion concentration at which its ionization is at a minimum), is much less stable in solution than in the presence of acid or alkali, as shown by Jacques Loeb.

Similarly, for an arsenious sulfide sol the hydrochloric acid of the acidified gelatin solution will drive back the ionization and force out of solution the hydrogen sulfide which is the stabilizing or peptizing agent of the arsenious sulfide particles.

On the other hand, when the inorganic colloid is present in large excess, the neutralization or the removal of a part of its stabilizing agent is not sufficient to throw it out of solution, while in the case of a large excess of oppositely charged gelatin, no precipitation ensues, due to the enveloping of the "neutralized" inorganic colloid particles by gelatin, which, by reason of its solution force, maintains the "neutralized" particles in suspension. The sign of the charge depends simply upon whether gelatin cations or anions are present, *i.e.*, whether it is an acidic or alkaline solution.

Hence when Billitzer mixed gelatin, ammonium hydroxide, and ferric oxide sol, in the order named, it is easily seen why he got flocculation. When he mixed acidified gelatin, ferric oxide sol, and ammonium hydroxide he did not get flocculation of the mixture because gelatin films had formed around the ferric oxide particles. Addition of ammonia merely changed the envelopes of cationic gelatin to gelatin anions. Had he, however, added the base slowly, he would have noted a point of very low stability of the gelatin-enveloped ferric oxide particles, namely at pH 4.7, the isoelectric point of this protein.

The sensitizing action of well-dialyzed albumin (Brossa and Freundlich) upon ferric oxide hydrosol can be explained similarly, since in neutral aqueous solution this protein is on the alkaline side of its isoelectric point, *i.e.*, it is negatively charged (anionic) and forms salts with the ferric ion of the stabilizing ferric salt, or causes hydrolysis of the latter, due to its combination with the hydrochloric or acetic acid in hydrolytic equilibrium with the stabilizing ferric salt of the ferric oxide hydrosol.

To summarize, a hydrophilic colloid will protect a less stable dispersion at all concentrations of the former, provided its sign of charge is like that of the latter. If it carries a charge of opposite sign, it will protect the less stable dispersion, if an amount in

excess of the isoelectric mixture is present. If added in amounts such as to give an isoelectric mixture, or less than the same, then the stability of the less stable dispersion will be decreased, possibly resulting in precipitation.

Various hydrophilic colloids show different protective effects. Zsigmondy[41] devised the "gold number" method as a means of defining the protective power of a given protective colloid. The "gold number" of a protective colloid is defined by Zsigmondy as the number of milligrams of the protective colloid which just fails to prevent the change of color of 10 cc. of red gold hydrosol to blue upon the addition of 1 cc. of a 10 per cent sodium chloride solution.

Zsigmondy prescribes the use of a gold hydrosol that shows a weak brownish opalescence to reflected light and a clear bright red color to transmitted light. It must not show even a trace of violet or blue. Such a sol was prepared by him in reducing gold chloride with formaldehyde.[42] A similar sol may be prepared by the Bredig arc method.

Zsigmondy's technique is as follows: Into three beakers, 0.01, 0.1, and 1 cc. of the protective colloid solution are pipetted and 10 cc. of gold hydrosol are added to each, followed by vigorous shaking for 3 minutes. Then 1 cc. of 10 per cent sodium chloride solution is run into each beaker while stirring. Assuming that change of color takes place in the first beaker and not in the others, the "gold number" is between the values represented by the amounts of protective colloid in 0.01 and 0.1 cc. For a more exact determination, the procedure is repeated on amounts between these limits. The number of milligrams of protective colloid which just fails to prevent the change in color of the red gold sol to violet is calculated as the "gold number."

The very different protective powers of the hydrophiles are seen in Table XVIII. In addition to Zsigmondy's value,[43] recent determinations by Gortner[44] are given.

[41] *Z. anal. Chem.*, **40** (1901), 697.

[42] *Liebig's Annalen*, **301** (1898), 30; ZSIGMONDY-SPEAR: "Chemistry of Colloids," John Wiley & Sons, Inc., New York, 1917, p. 90.

[43] *Z. anal. Chem.*, **40** (1901), 697; ZSIGMONDY-SPEAR: pp. 107, 212.

[44] *J. Am. Chem. Soc.*, **42** (1920), 595.

TABLE XVIII

Colloid	Gold number	
	Zsigmondy	Gortner
Gelatin	0.005–0.01	0.005–0.0125
Isinglass	0.01 –0.02	
Casein	0.01	
Egg albumin	.....	0.08–0.10
"Protalbinic acid"*	0.03 –0.08 (Na salt)	0.15–0.20
"Lysalbinic acid"*	0.02 –0.60 (Na salt)	0.10–0.125
Gum arabic	0.15 –0.5	0.10–0.125
Gum tragacanth	About 2	
Dextrins	6–20	
Dextrin (British gum)	.....	125–150
Soluble starch	.....	10– 15
Potato starch	About 25	
Sodium oleate	0.4–1	2– 4

* These are protein degradation products so named by Paal (*Ber.*, **35** (1902), 2195), prepared by heating egg albumin in alkaline solution and precipitating by acetic acid. He uses these products in the preparation of protected metallic dispersions.

These numbers are useful as rough indices of relative protective powers only. Probably the concentration and degree of dispersion of the gold sol influence the result. The pH of the solution used certainly will affect the values. If the protective colloid solution is slightly acid, it will show a poorer protective action than one which is neutral or slightly alkaline. One sample of gelatin tested by the writer precipitated the gold sol.

The protective effect is not instantaneous. Some time must elapse after mixing for the optimum effect. Three minutes' time is usually sufficient. Dilution is also a factor. In a certain case, Zsigmondy found that 0.015 mg. of gelatin in 23 cc. of water did not protect 10 cc. of a gold hydrosol, but, when added in 3 cc. volume and then diluted with 20 cc. of water, it did protect the sol. Apparently, when protection has taken place, dilution does not affect it.

The degree of dispersion of the protecting colloid also affects its gold number as shown for gelatin by Menz[45] and by Elliott and Sheppard.[46] This is shown clearly by the experiments of the latter. Solutions of gelatin were prepared as follows:

1. By making up the solutions directly without subsequent dilution, as 1 g. gelatin to 100 cc. solution for a 1 per cent solution, to be heated for 4 hours at 50°C. to establish equilibrium, and cooled in a water bath at 20°, at which temperature all gold numbers were determined.

2. By making an original solution of 1 per cent, heating at 50° for 4 hours, cooling, and diluting to 0.01 and 0.001 per cent at 20°.

3. By making the original solution of 1 per cent at 50°, heating for 4 hours, and making further dilutions of 0.01 and 0.001 per cent at 50°, with a further 2-hour heating to equilibrium and cooling at 20°.

TABLE XIX

Strength of solution, per cent	Gold number
Original	
1.0	0.15
0.01	0.02
0.001	about 0.015
Diluted at 50°	
0.01	0.0075
0.001	0.02
Diluted at 20°	
0.01	0.0075
0.001	0.02

[45] *Z. physik. Chem.*, **66** (1909), 129.
[46] *J. Ind. Eng. Chem.*, **13** (1921), 699.

The results shown in the table clearly indicate that the gold number decreases with decreasing concentration, that is, the protective action of the gelatin increases with decreasing concentrations. This is in agreement with the work of Menz. The protective action is not increased by a decrease in the quantity of gelatin, but, as the concentration is lowered, the state of division of the gelatin present is altered. At high concentrations there is a majority of large particles with some smaller particles also; at low concentrations, a majority of very fine particles and very few of the larger particles. The larger jelly particles exert very little, if any, protective action. It is evident that gelatin must be completely in solution to show its maximum protective effect.

Elliott and Sheppard also found that the gold number of gelatin solutions increases upon standing, which is concomitant with decrease in degree of dispersion of the gelatin. After determining the gold numbers of 17 different gelatins of all grades and methods of manufacture, they conclude that this method is of little or no value in the grading of gelatins. The gold numbers differed but little and the classification thus made possible was too rough, bearing no simple relation to those properties which are of chief interest to users of gelatins.

Heubner and Jacobs[47] have tried to determine the gold numbers of purified blood proteins (albumin, globulin, and hemoglobin), but found that the gold number of a given protein varied with the method of preparation. Some of their samples caused the gold sol to turn violet in color. This was undoubtedly caused by a lack of pH control. Reitstötter[48] claims that the gold numbers of the various fractions of sera from a number of animals, both normal and diseased, are characteristic in most cases, the pathological condition of the animal influencing the same. It is interesting to note that he finds that the relative protective action, expressed as gold number, is altered by the acidity of the medium.

The gold numbers of a series of protein degradation products, such as proteoses, peptones, etc., have been determined by Zunz.[49] Attempts have been made to apply the gold number

[47] *Biochem. Z.*, **58** (1914), 352.

[48] *Oesterr. Chem. Ztg.*, **25** (1922), 29 through *Chem. Abs.*, **17** (1923), 290.

[49] *Archives internat. de Physiol.*, **1** (1904), 427; **5** (1907), 111, 245; *Bull. Soc. Roy. des Sci. med. et nat.*, **64** (1906), 187; ZSIGMONDY-SPEAR, pp. 108–109.

method to analysis of urines. The presence of protective substances in urines have been found,[50] but it is doubtful whether the method can have any diagnostic value, for reasons already shown in other instances. Furthermore, Ottenstein[51] has been unable to find characteristic gold numbers in urines from certain pathological cases. He finds that the gold number of the well-dialyzed solids of normal urines range from 3.5 to 7.0, while in disease, fluctuating values are found both above and below the normal values and not at all characteristic for any one pathological condition.

Protective colloids inhibit the decomposition of hydrogen peroxide by platinum hydrosol. Groh's determinations[52] of the effect of gelatin, gum arabic, and dextrin are shown in Table XX. The time for 50 per cent decomposition of a given amount of hydrogen peroxide by a fixed quantity of platinum hydrosol was determined both in the absence and presence of varying amounts of protective colloid by means of permanganate titrations of samples of the mixture withdrawn at given intervals.

TABLE XX

Protective colloid	Time for 50% decomposition, minutes	Protective colloid	Time for 50% decomposition, minutes
None	20		
0.1% Gelatin	265	0.001% Gelatin	103
0.1% Gum arabic	86	0.001% Gum arabic	21
0.1% Dextrin	66	0.001% Dextrin	23
0.01% Gelatin	150		
0.01% Gum arabic	39	0.0001% gelatin	71
0.01% Dextrin	28		

[50] LICHTWITZ and ROSENBACH: *Z. physiol. Chem.*, **61** (1909), 112; LICHTWITZ: *Ibid.*, **64** (1910), 144; SALKOWSKY: *Berlin klin. Wochenschr* (1905) (through ZSIGMONDY-SPEAR, p. 111).

[51] *Biochem. Z.*, **128** (1922), 382.

[52] *Z. physik. Chem.*, **88** (1914), 414.

The order of effectiveness in inhibition of the catalysis is seen to be the same as that of protective powers shown by the Zsigmondy gold numbers. Confirmation of Groh's results is found in a recent paper by Iredale[53] where the "inhibition number," *i.e.*, that percentage of protective colloid which is just insufficient to inhibit the catalytic action of colloidal platinum upon hydrogen peroxide, is found to run parallel to the gold number (Table XXI).

TABLE XXI

Colloid	Gold number	Inhibition number	Gold number ratios	Inhibition number ratios
Gelatin	0.02	2×10^{-6}	100.	100.
Egg albumin	0.1	1×10^{-5}	20.	20.
Dextrin	3.	2×10^{-4}	0.66	1.
Starch	5.	6×10^{-4}	0.40	0.33

TABLE XXII

Protective colloid	Series I		Series II	
	k	Ratio	k	Ratio
None	0.055	1.00	0.025	1.00
Gelatin	0.0059	0.11	0.0044	0.18
Glue	0.0072	0.13	0.0056	0.22
Egg albumin	0.0094	0.17	0.007	0.28
Gum arabic	0.035	0.64	0.020	0.80
None	0.083	1.00	0.018	1.00
Gum tragacanth	0.028	0.34	0.013	0.72
Egg albumin	.....	....	0.0057	0.32
Gum arabic	0.043	0.52		
Dextrin	0.031	0.37		
Starch	0.041	0.50		

[53] *J. Chem. Soc.*, **121** (1922), 1536.

A summary of a series of measurements made by Iredale[54] upon the decomposition of hydrogen peroxide $\left(\frac{M}{40}\right)$ by platinum hydrosol (Bredig) at 25°C. is given in Table XXII. The results are expressed in terms of k, the monomolecular reaction velocity constant. In "Series I," 0.01 per cent and, in "Series II," 0.001 per cent of protective colloid was present. The mixture of platinum sol and protective colloid was always allowed to stand 15 minutes before adding to the hydrogen peroxide.

The effect of varying concentrations of gelatin upon the activity of the platinum hydrosol in a mixture containing $\frac{1}{30{,}000}$ gram atoms of platinum per liter of mixture is given in Table XXIII. Iredale explains the inhibitory effects of the protective

Table XXIII

Gelatin, Per Cent	k
None	0.0151
0.005	0.0027
0.001	0.0031
0.0001	0.0043
0.00005	0.0050
0.00001	0.0107
0.000005	0.0140
0.000001	0.0151

colloids "on the ground of selective adsorption resulting in a decreased concentration of hydrogen peroxide at the platinum surface . . ." In other words, he attributes it to the formation of films of protective colloid about the platinum particles, in accordance with the envelope theory of protective action suggested by Bechhold.

The envelope theory of protective action has been definitely proved by Jacques Loeb[55] by a comparison of the stability of protein solutions with that of dispersions of protein-coated collodion particles. He prepared collodion suspensions by dissolving dried collodion in pure acetone, adding water to appearance of turbidity, and distilling off the acetone under reduced pressure, whereupon a creamy suspension of collodion particles

[54] *J. Chem. Soc.*, **119** (1921), 109.
[55] *J. Gen. Physiol.*, **5** (1922–23), 479.

was obtained.[56] The preparation of protein-coated collodion particles was suggested by his previous experience with collodion membranes,[57] where he found that:

> When collodion membranes are filled with a 1 per cent solution of a protein, such as gelatin, crystalline egg albumin, casein, or oxyhemoglobin, there is formed overnight inside the membrane a durable film of solid protein which cannot be washed away, even if the interior is rinsed out as often as ten or twenty times with warm water. This film betrays itself by its color in the case of oxyhemoglobin. The forces which make the film adhere to the collodion must be very strong, but they do not depend upon the ionization of the protein, since the films are formed no matter whether the protein is at the isoelectric point, or whether it is on the alkaline or on the acid side of the isoelectric point. The forces which cause the film formation must be those forces of secondary valency responsible for phenomena of adhesion and cohesion in general.[58]

Loeb allowed a small quantity of collodion suspension to remain overnight in an aqueous solution of a protein. The next morning the particles were centrifuged from the protein solution and made up to a creamy suspension in water at a desired pH. This suspension of protein-coated particles was added to various salt solutions to note the behavior. The effects of various salts were followed by electrophoresis measurements and observation of the concentrations of a given electrolyte which caused precipitation. It was found that the conduct of the protein-coated particles is identical with that of a solution of the protein. The concentrations of different salts required to precipitate suspensions of gelatin-coated collodion particles in water are practically identical with the concentrations of the same salts required to "salt out" gelatin from aqueous solutions. Furthermore, Loeb found that just as the solubility of gelatin at its isoelectric point (pH 4.7) is increased by the addition of certain kinds and amounts of salts, so are gelatin-coated collodion particles rendered more stable when protected by isoelectric gelatin.

[56] *J. Gen. Physiol.*, **5** (1922–23), 109.

[57] *Ibid.*, **2** (1919–20), 577.

[58] This conduct is like that of gold foil in gelatin solutions observed by Zsigmondy as early as 1900 (Zsigmondy-Spear, p. 112). Gold foil covered itself with a film of gelatin that could not be removed by boiling water. This layer prevented the amalgamation of the gold with mercury.

Loeb noted a peculiar behavior in the case of egg albumin. He found that it is not a good protective colloid for collodion suspensions. Investigation of the properties of albumin-coated collodion particles showed them to be practically identical in stability to that of suspensions of denatured (heat-coagulated) albumin particles. He believed that when egg albumin forms a film of its solution around collodion particles, the albumin molecule undergoes a rearrangement or orientation to render its water-soluble groups ineffective. He recalled the observation of Ramsden[59] on the films of certain proteins which form in aqueous solutions, due to the lowering of the surface tension of water. Ramsden said that some of these films undergo irreversible coagulation. It is likewise well to recall that mechanical grinding of a dry powder of soluble blood albumin renders the albumin insoluble.[60]

The writer would point out that deposition of albumin at an interface as a result of its lowering the interfacial tension does not always result in irreversible coagulation or denaturing. When an aqueous solution of albumin is shaken with chloroform, Ramsden's so-called "mechanical coagulation" appears, *i.e.*, solid films of albumin form at the water-chloroform interfaces and settle out. Nolf[61] finds that the albumin is chemically unaltered in this instance.

Loeb also found casein and edestin to be poor protectors for collodion particles. He defines protective colloids as follows:

> Protective colloids must be capable of forming a durable film on the surface of suspended particles and the molecules constituting the film must have a higher attraction for the molecules of the solvent than for each other; in other words, they must possess true solubility. Only in this case can they prevent the precipitating action of low concentrations of electrolytes on particles which are kept in suspension solely by the high potentials of an electrical double layer. Thus, gelatin films, in which the attraction of the molecules for water is preserved, have a general protective action, while crystalline egg albumin, casein, and edestin, which seem to lose their attraction for

[59] *Proc. Roy. Soc.* (London), **72** (1903), 156.

[60] Herzfeld and Klinger: *Biochem. Z.*, **78** (1917), 349; Wiechowski: *Ibid.*, **81** (1917), 278 (through Loeb: *loc. cit.*).

[61] *Réunion soc. belg. biol.* (1921), 273 (through *Chem. Abs.*, **16** (1922), 2874.

water when forming a film, have a protective action only under limited conditions.

Beans and Beaver[62] have performed an experiment which shows that the protection of colloidal gold by gelatin is due to adsorption of the gelatin by the gold particles. They found that the gold particles of a red gold hydrosol (Bredig) were completely precipitated by centrifuging for 3 minutes at a force equivalent to 32,000 times gravity. The precipitate was black and irreversible. Centrifuging a mixture of 5 cc. of a 0.1 per cent gelatin solution and 50 cc. of the gold sol resulted in deposition of the gold particles in 16 minutes, but the precipitate was red in this instance and could be redispersed to a red sol upon shaking with water. On heating some of this precipitate it showed a slight charring, indicating the presence of gelatin. The same concentration of pure gelatin showed no precipitation of gelatin even after 30 minutes' centrifuging at 32,000 "times gravity."

The envelope or adsorption theory of protection seems to be fairly well established. Rideal,[63] however, states, as a result of hydrogenation experiments, that the protective colloid peptizes (*i.e.*, disintegrates and increases degree of dispersion) the metallic sol particles, which confirms Bancroft's hypothesis.[64] In the hydrogenation of phenyl propiolic acid, utilizing both platinum and palladium hydrosols protected by gum arabic, as catalysts, Rideal found that the protected sols showed greater activity than the unprotected ones. There was an optimum amount of gum arabic beyond which the activity fell below that of the unprotected sols. Rideal ascribes this to increase in the specific surface of the colloidal metal particles due to "peptization" by the gum. Examination of his paper reveals the fact that the sols were prepared by adding sodium carbonate to platinum or palladium chloride, then gum arabic, and, finally, reducing with hydroxylamine. Apparently, the fact that the gum might act otherwise than as a "peptizing" agent seems to have been ignored as well as the effect of the reaction products other than the colloidal metal. It might be mentioned here that Pearce and O'Leary[65] find that gum arabic inhibits the hydrolysis of

[62] Beaver, D. J.: Dissertation, Columbia University, 1921.
[63] *J. Am. Chem. Soc.*, **42** (1920), 749.
[64] *J. Phys. Chem.*, **20** (1916), 85.
[65] *J. Phys. Chem.*, **28** (1924), 51.

methyl acetate. They ascribe this to the adsorption of the catalyst, hydrochloric acid, by the gum as shown by pH determinations.

The majority of the investigations on protective colloids have been made upon aqueous dispersions, as is to be expected, but it is well to bear in mind that their usefulness is not restricted to water solutions. Bancroft[66] points out that aniline dyes which are insoluble in benzene can be dispersed therein by the aid of a benzenophilic colloid, such as zinc or magnesium resinate, and thus be used in lacquers.

A practical use of protective colloids is shown by Wegelin,[67] who found that the adhesion of metallic particles in grinding could be overcome by the presence of an aqueous gelatin solution.

Protective colloids have been found useful in the manufacture of ice cream, their presence preventing the formation of large ice crystals and thus insuring smoothness. They have been erroneously called "fillers" in this application. Gelatin, egg albumin, and karaya gum are the most popular colloids for this purpose. A discussion of the effect of gelatin in ice cream is given by Alexander.[68] The latter has also observed that the presence of protective colloids in milk prevents the formation of lumpy curd when the milk is acidified.[69]

The presence of protective colloids is avoided in analytical chemistry, since it has been known, long before they were recognized as such, that their presence prevented the precipitation of insoluble compounds. For example, Pauli and Samec[70] have found that a number of insoluble compounds are more soluble in protein solutions than in water. An enumeration of the many instances reported would not serve any useful purpose here.

Before closing, it should be noted that protective action, *i.e.*, stabilizing rather unstable particles in solution, is not limited to the proteins, gums, soaps, etc. Inorganic dispersions frequently

[66] *J. Phys. Chem.*, **24** (1920), 21.
[67] *Kolloid-Z.*, **14** (1914), 65.
[68] *Kolloid-Z.*, **5** (1909), 101.
[69] *Ibid.*, **6** (1910), 197; Alexander and Bullowa: *J. Am. Med. Assoc.*, **55** (1910), 1196; *Archives of Pediatrics* (1910), 17.
[70] *Biochem. Z.*, **17** (1909), 235.

act as stabilizing agents, but the writer is not so confident that in such cases, as noted below, the action is due to film formation.

According to Bancroft, hydrous chromium oxide adsorbs the hydrous oxides of iron, nickel, cobalt, manganese, and copper and, consequently, protects them to a certain extent, making them apparently soluble in potassium hydroxide solution. When the chromium salt is in large excess relatively to the other salt present, none of the other hydrous oxide is precipitated when not too great an excess of alkali is added, but, when the other salt is in excess, everything is precipitated upon addition of alkali, chromium oxide being adsorbed and carried down in the precipitate. Bancroft refers to the protective action of the uranyl salt of molybdic acid. Tungstates are precipitated by uranyl salts while molybdates are not. If a uranyl salt is added to a solution of a molybdate and tungstate, nothing is precipitated if the molybdate is in excess, while practically all the molybdate is carried down when the tungstate is present in excess.

In the tables showing the mutual precipitation of inorganic colloids early in this chapter, it was seen that when a small amount of one colloid was mixed with a large amount of another, no precipitation took place. The former lost its stabilizing agent, to be sure, through chemical action with that of the latter (it was neutralized), but remained dispersed, due to combination with the particles of the latter.

CHAPTER XIV

ENZYMES

By

E. Frankland Armstrong

Enzyme action, in reality, is an interaction in which water is either distributed upon a single molecule, which is thereby resolved into two others

$$A.O.B + H.OH = A.OH + B.OH$$

or is divided between two molecules in such manner that, while the one is hydroxylated, the other is hydrogenated

$$A + 2H.OH + B = A(OH)_2 + B.H_2$$

The study of enzyme action is thus, at bottom, a study of water, to the chemist the most elusive of all substances. Enzymes themselves are part of a larger colloid complex and the actions in which they take part are all actions at a surface, as distinct from action between substances like acid and alkali in true solution. The investigation of surface action is thus the primary task if we are to understand enzymes.

Enzymes are regarded as catalysts, but we are still largely in the dark as to their real nature; much is known as to the extent and manner of their action, and it has been customary to think of them as definite chemical entities, though it is probable that the catalytic activities associated with them are to be connected with definite aggregates of groups in a larger molecule, with the consequence that the enzyme, as such, is incapable of existing. Their activity in the main is hydrolytic, that is, they render water molecules active. We define a catalyst as the agent which brings about the inclusion of the interacting substances in a circuit within which change takes place as soon as

the circuit is established; it may also be the actual agent by which the change is effected.

Enzymes are present in animal and vegetable tissues, from which they are obtained in a concentrated rather than a pure condition by a variety of methods involving, in the first place, the rupture of the cell wall, and then sometimes the decomposition of a larger complex to liberate the active enzyme, such as is best effected by self-digestion or autolysis. The enzyme is precipitated by cautious addition of alcohol or acetone, redistributed in a little water, and the precipitation repeated, if desired. Without going into details well known to workers in these fields, all the practical methods are such as avoid drastic treatment likely to destroy colloid aggregates or, in a word, affect surface, which the writer regards as the prime essential for an active enzyme. It will be gathered from the above that enzymes are relatively unstable and less active under laboratory conditions, and the critically minded will treat with caution results obtained with too highly purified, that is, overtreated, products from the point of view of the explanation of their behavior as colloids.

Enzymes are active in liquids which have been filtered—hence, the term "soluble ferments" long applied to them—but they are also active in the insoluble state both in aqueous solutions and other media. They are non-diffusible through parchment paper. The outstanding property of enzymes which distinguishes them from all other catalytic agents is their specifically selective nature; any explanation of their behavior must take this into account. Indeed, far from being exaggerated, as stated by Bayliss in his British Association report (1918), this selective and limited action is one of the outstanding factors in the regulation of metabolism in living matter and its importance has been imperfectly understood by many writers on enzyme action.

In general, catalysts become more and more active as the extent of their surface is increased. A lump of metallic nickel, for example, is almost inactive in promoting reduction, but particles obtained by abrasion become more active as their size diminishes. Metal in the very finely divided particulate or colloid state, as it is termed, is very active, and a still finer state of division and

greatest activity is obtained by precipitating nickel from a dilute solution of its nitrate on the surface of an inert carrier, such as kieselguhr, and afterwards reducing the oxide so formed at a suitable low temperature to metallic nickel. One gains the mental picture of a film made up of extremely small particles extending over the surface of the interstices of a sponge-like carrier so that each particle is able to come into actual contact with gas or liquid. Loss of activity is observed when the temperature of preparation has proved to be too high, thereby causing the particles to coalesce and reduce the amount of surface.

Now, enzymes are essentially particulate colloids in an even finer state of division or, more correctly, dependent even more on surface conditions than the active metal catalysts. The accumulated knowledge of the methods of preparation of an active enzyme, the care which is necessary with regard to temperature, time of extraction, reaction of the medium, presence of inorganic salts and of various poisons affords very definite evidence that in chemical phraseology the enzyme is very unstable or, in other words, its active surface must not be impaired. Enzymes are not used on supports like metals, but the large molecules of which they are only a section themselves act in this fashion. The pseudosoluble colloid enzymes are not in a state of true dissolution but are able to develop the maximum surface area, probably even more so than the most active metallic catalysts and certainly infinitely more than other inorganic catalysts which act as hydrolytic agents. This fact offers a ready explanation of the phenomenal activity of enzymes compared with other chemical agents under like conditions of temperature.

The action of the majority of the really authenticated enzymes is hydrolytic; the following classes have been studied:

Saccharo-clasts, such as diastase, invertase, maltase and lactase, which act on starch and the dissaccharides, and emulsin, which attacks many natural and artificial glucosides.

Lipoclasts, which split fats into glycerol and fatty acids.

Proteoclasts, which break down proteins and polypeptides into their constituent amino acids.

Urease, which hydrolyzes urea to ammonia and carbon dioxide.

Oxidase, reductase, catalase, concerned in biological oxidations and reductions.

An examination of each of these processes follows in such detail only as will serve to emphasize certain of their general and specific behavior as colloids.

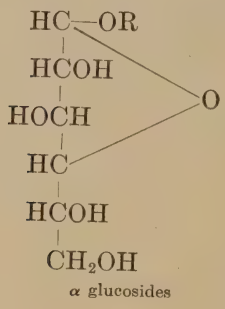
Saccharo-clasts

The literature relating to these is so extensive as to have lost its value unless very critically studied. Much of the work recorded has been done without a full understanding of the necessary technique, so that in many cases the measurements recorded are those of the influence of secondary disturbing factors and not of the enzyme itself. Two facts have been definitely established, the one that the action of the enzyme is absolutely selective, one enzyme acting on β-glucosides alone, another on β-galactosides only, and a third on α-glucosides only, while invertase acts only on cane sugar. The selective action is connected only with the sugar part of the molecule, the effect of the non-sugar radicle being merely quantitative and secondary. The second fact is that all the observed behavior of these enzymes, when studied quantitatively, is in agreement with the idea that action takes place at a surface and that under ideal conditions, with a regular access of substrate and regular removal of products and the elimination of all poisons, action takes place at a steady rate in conformity with the hypothesis that it is preceded by the formation of an additive complex of enzyme and sugar.

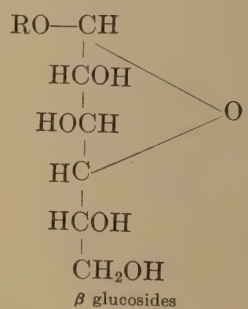
Equal amounts of substance are hydrolyzed in successive equal intervals of time, that is to say, the course of action is expressed graphically by a straight line. On the contrary, when cane sugar is hydrolyzed by acid, the action is in accord with the laws of mass action and is expressed by a simple logarithmic curve. Numerous workers have sought to force mass action laws into use in interpreting enzymic action, believing that the analogy between the acid catalyst and the supposed soluble enzyme catalyst was complete, and ignoring the great difference between the character of the two actions. It is desirable to emphasize, therefore, that the more nearly the proper effect of the enzyme is understood the more it is seen to depart from the mass action "laws," thus showing that it is not uniformly distributed but itself a focus of attraction and concentration. The rate of

change is definitely linear in cases where the hydrolysis is all but complete, as is best exemplified in the case of urease; the rate diminishes when there is reversal, as in the case of lipase. The ideal conditions demanded to illustrate this hypothesis are often difficult to realize in the laboratory, but they undoubtedly obtain under natural conditions in the cell.

It is desirable very briefly to illustrate the selective nature of enzymes. As the graphic formulas show, the only difference



α glucosides



β glucosides

between α and β glucosides is in regard to the arrangement of the groups attached to the topmost carbon, here shown as placed to the right and left of the carbon chain. Yet maltase acts on α glucosides alone, emulsin on β glucosides alone. By the interchange of the H and OH groups attached to either of the four next carbon atoms of the chain, isomeric sugars are obtained, *e.g.*, mannose, galactose, gulose, etc. In no case are the glucoside derivatives hydrolyzed by either maltase or emulsin By well-known methods the chain of carbons has been shortened or lengthened and other sugars and their glucoside derivatives prepared. In no case are they acted on by these two enzymes. As we have recently learned, some of the changes mentioned involve an alteration in the position and magnitude in the oxygen ring which may contain three, four, or five carbon atoms in addition to oxygen; these changes also render the enzymes incompatible with the glucosides. This subject has been studied in great detail, but it is unnecessary to multiply examples; the proof of the selective action is absolute.

Lipase

Lipase, first discovered in the germinating seeds of *Ricinus communis*, is present in many seeds, usually in the germinating rather than the resting stage, its function being to make the fats stored up in the seed available for the growing embryo. Animal lipase is present in most tissues, especially the liver; it appears to cling to the solid particles of tissue cells. It is very doubtful if active filtered extracts of the enzyme can be obtained; vegetable lipase, in particular, is very sparingly soluble in water. The experiments of H. E. Armstrong, Connstein, Kastle, and Loevenhart, amongst others, have shown that vegetable lipase acts preferentially on natural fats, other ethereal salts being but little attacked by it; animal lipase, on the other hand, is quite active in hydrolyzing simple esters, but acts on the natural fats with difficulty. Such difference is probably more apparent than real, and is due to the difficulty of securing a satisfactory emulsion.

In other words, the activity of the colloid enzyme is dependent on proper association with the fatty material; in the liver, lipase and fat are in close conjunction, not suspended in water.

Probably vegetable lipase powder (Tanaka) contains an emulsifying constituent on which its activity is in no small measure dependent. H. E. Armstrong and Gosney have suggested that the properties of lipase are to be accounted for on the assumption that it is a colloid molecule possessed of a carboxylic or even a phosphoric group so situated that it cannot be self-neutralized but yet sufficiently near to a basic center to be interfered with by any acid which can combine with this latter. The interaction must be supposed to take place at and between surfaces separated at most by a thin, almost molecular, film of water. Presumably the rate at which interaction takes place is dependent on the conditions at the colloid surface; as these cannot be expressed in terms of the concentration of the solution, it is impossible to apply the laws of mass action to the interpretation of the changes observed. As previously explained, under ideal conditions equal amounts of material will be hydrolyzed by a given quantity of enzyme in successive equal intervals of time; in practice, numerous secondary causes may effect departure from this rate.

Urease

This enzyme, which is the cause of the alkaline fermentation of urea, is present in certain microorganisms but was not investigated to any extent until its discovery in the soybean and in various leguminous seeds made a plentiful supply available. Its action, like that of other enzymes, is essentially specific, it being entirely without action on substituted ureas. The addition of ammonia has a retarding effect on the hydrolysis, while the presence of carbon dioxide accelerates the activity of the enzyme.

The prevailing view as to the mechanism of action of the enzyme, is that, in the first place, there is a combination between urease and the substrate followed by disruption of the combination with liberation of the urea as ammonia and carbon dioxide. The ease with which measurements can be made has rendered urease an ideal material for studying the course of enzyme action, which has been done by H. E. Armstrong and Horton and subsequently by Van Slyke. The work of the former investigators amply justifies the belief that enzymic action takes place entirely at the surfaces of colloid particles suspended in the solution of the hydrolyte and not between substances which are all in true solution. This hypothesis hardly differs from the original suggestion of H. E. Armstrong and Horton in 1912, who regarded urease as a feebly acidic substance uniting with the feebly basic substance urea before it can produce change. The presence of ammonia, a more basic substance, interferes with such union and, consequently, retards change.

The enzyme solution is prepared from the fat-extracted, ground soya meal by digestion with water and simple filtration; any attempts to purify the enzyme and to free it from the large amount of albuminous matter resulted in less active preparations.

Oxidases

The numerous changes in the living body involving oxidation and reduction are attributed to enzymes. Molecular oxygen is quite unable to burn the substances which are so easily dealt with by the tissues of the body, and yet it is in this form that the oxygen reaches them. One conception of oxidases, based on the

views of Bach, Bertrand, and Engler, is of a system consisting of an organic substance capable of taking up molecular oxygen to form a peroxide and parting with one or even both atoms to another substance, the transference being determined or accelerated by a peroxidase. In the plant, as Miss Wheldale has shown, catechol derivatives are capable of acting in this manner.

Many biological oxidations take place in aqueous solution in the absence of molecular oxygen, provided a reducing substance is also present—the oxygen is derived by the splitting of water, one substance, termed the "hydrogen acceptor," suffering reduction, and another, the "oxygen acceptor," being simultaneously oxidized. In practical work methylene blue is very commonly added as an extraneous hydrogen acceptor, the disappearance of color establishing that the oxidative change has taken place.

Biological oxidation is thus essentially a process of splitting water into hydrogen and oxygen. If A is the substance oxidized in vitro we have, under anaerobic conditions

$$A + 2\ H.OH + B \rightarrow A(OH)_2 + BH_2$$

and under aerobic conditions

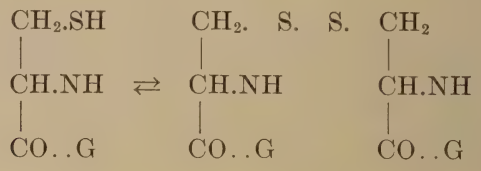
$$A + 2\ H.OH + O_2 \rightarrow A(OH)_2 + HO.OH \rightarrow AO_2 + 2H_2O$$

A number of substances are oxidized by catalysts derived from living tissues under either anaerobic or aerobic conditions, there being evidence to show that the same catalyst controls both processes. There is, however, an increasing amount of evidence that the catalysts are in many cases specific in relation to the substrate, and it must, therefore, be assumed that in this case also there is some structural relation between enzyme and substrate and that the formation of an additive complex is a prelude to action.

The most recent summary of this subject by Hopkins, which has been freely drawn upon in making this abstract, emphasizes the diverse character of the catalytic systems which control biological oxidations. They differ largely in stability, some displaying the characters of enzymes in ordinary colloid suspension, whereas others are more closely associated with solid structures in the cell. In addition, the cell undoubtedly contains catalytic agents able to constitute oxidizing systems which are

both more stable and also thermostable and not to be classed as enzymes—such are iron compounds.

Hopkins attaches particular significance to the disulfide and thiol groups which in the cell suffer reversible oxidation and reduction. A dipeptide, glutathione, present in most actively living tissues, discovered by him, consists of glutaminic acid condensed with cystein or, in the oxidized form, with cystine. The two forms may be represented as follows, G standing for a glutaminic acid nucleus attached either to the amino or carboxyl groups.



It is of some physiological significance that in the case of the dipeptide both the disulfide and thiol form are freely soluble in the tissue fluids, whereas cystine is not. Hopkins has shown that in the living tissues the thiol group of glutathione is autoxidizable, while the disulfide group thus formed is under similar conditions freely reducible to the thiol form by factors present in the tissues.

The exact explanation of all the observations made by Hopkins in connection with this reaction is still under investigation and the reader is referred to the original literature, but it is possible to indicate that compounds, such as glutathione, forming part of a polypeptide which, in turn, is part of a larger colloid complex, may well represent centers of enzymic activity in such molecules.

As an example of the selective nature of oxidases, the work of Morgan, Stewart, and Hopkins may be quoted, showing that an enzyme present in the liver tissue and in milk is able, under aerobic conditions, in presence of methylene blue as hydrogen acceptor, to oxidize hypoxanthin at exactly twice the rate that it oxidizes xanthin, the product of oxidation being uric acid in each case. Under anaerobic conditions uric acid is produced at the same rate from both compounds. Closely related substances, such as guanine, caffeine, uracil, thymine, histidine, etc., are not oxidizable under these conditions. The oxidation has been shown

to proceed at a linear rate, indicating that the nitrogen compounds are held at the surface of the enzyme and not released until fully oxidized.

Having illustrated certain features in the behavior of the individual enzymes, it is possible to elaborate with some certainty a more general conception of the manner of their action. In doing so, however, it is necessary to touch on several subjects of a controversial nature.

In the first place, an enzyme has a double function, that of attracting or holding the hydrolyte and that of determining its hydrolysis. It acts both as an *acceptor* and as an *agent*. Some writers would deprive it of the latter function, believing that when the hydrolyte is suitably held—forming a part, it may be, of an electrolytic circuit—certain other forces come into play or, perhaps, the water molecules themselves become active as hydrolytic agents. The difference between the two theories is more one of detail than of consequence and the question is one which is ripe for immediate further investigation.

The activity of an enzyme as an acceptor is the basis of our hypothesis. In no other way can the highly selective character of enzymes, as is especially illustrated in the case of the saccharoclasts, be explained. It is, then, a natural corollary that this close relationship between enzyme and hydrolyte involves a similarity in structure; enzyme and hydrolyte must contain the same groupings, no doubt as part of a much larger molecule. It has been suggested, for example, that the glucoside-splitting enzymes contain all or part of the glucose skeleton; lactase is, perhaps, akin to galactose; invertase may have the whole cane sugar structure or that part involving the junction of glucose and fructose residues, the exact nature of which still baffles us; lipase may contain a carboxylic grouping; urease such a residue as arginine. Such conjectures still lack experimental proof. The crude enzymes contain such elements as suggested, but their purification is at present impossible. At all events, the hypothesis involves the assumption that the relationship of the acceptor section of the enzyme to the hydrolyte is that of a superposable and, therefore, practically identical radical. This explanation goes somewhat further than Emil Fischer's lock-and-key conception, which is generally pictured as a close fitting

of the enzyme and substrate molecules, like the pieces of a jigsaw puzzle.

The conception of the enzyme holding the hydrolyte demands further consideration as to the nature of the attachment. There may either be formed a loose intermediate complex, depending on the attraction of similar grouping for one another or on the partial valencies exercised by oxygen and nitrogen atoms, or, as some would prefer, the hydrolyte is concentrated, absorbed, adsorbed, or in some other way held at the surface of the enzymes. The nature and behavior of such intermediate complexes is best left for consideration in another paragraph.

The only hydrolytic agents known to us are acids or alkalies, so that it is fair to assume that if the enzyme acts as an *agent*, it does so in virtue of the colloid aggregate containing an acid radicle so situated with reference to the acceptor section that the hydrolyte, when combined or associated with this, is in immediate proximity or sufficiently near to enable a conducting circuit to be set up. It is an outstanding experimental fact in connection with hydrolytic enzymes that they are very sensitive to alkalies; it is impossible to be too careful to exclude alkaline impurities and all work must be carried out in hard glass utensils, using bottles, pipettes, and measuring vessels of the same material. For the same reason, the addition of amphoteric substances, such as glycine, is often of advantage.

It is generally accepted that at a colloid surface in water the water molecules are in a state of greater activity than the average activity of the water in the neighborhood: whereas the normal water molecule is a complex (H_2O), it is probably the simple molecules H_2O which are active in chemical change and which, therefore, are attached to the surface of the colloid. As a consequence of this property of the surface, the molecules of hydrolyte are absorbed from the solution and concentrated at the surface. If the active section of the enzyme is only a portion of the whole colloid aggregate, it probably remains highly charged with the hydrolyte almost up to the point at which the supply in the solution is exhausted, the rate at which liquid diffusion takes place being so great that the supply of hydrolyte to the surface is not a limiting factor. A constant supply of hydrolyte is, accordingly maintained at the surface of the enzyme.

Alternatively, on the intermediate complex theory, they are attracted to the surface and loosely combined with it. Under either hypothesis no state of fixity is imagined. The loose intermediate complex is continually being formed and broken down again; the absorbed hydrolyte is not permanently held, but oscillates between it and the liquid of which the water molecules also exercise a pull on the soluble hydrolyte. Consequently, only a certain proportion of effective contacts are made; it is the number of these in the unit of time which determines the rate of hydrolysis.

Normally, when two substances, such as sugar and acid, act on one another in aqueous solution, the solvent water exercises an attraction for both which, in the case of acid, is so great that only a small fraction of the total present is able to make effective contact with the sugar. Hence, the apparent low activity of acids as hydrolytic agents. In the case of the colloid enzyme, water has very little attraction and, as the colloid is in a finely divided state, which is equivalent to the maintenance of the largest possible amount of surface, the hydrolyte tends to accumulate at the surface and the attractive influence of the solvent water is largely overcome. That is to say, a relatively large proportion of the hydrolyte is brought into effective conjunction with the enzyme agent which is placed under specially favorable conditions.

We have assumed elsewhere that the carboxylic radicle is the agent; this, though only weak in the majority of acids, has a high efficiency in some, as, for example, the substituted acetic acids, and it may be especially powerful in the enzymes.

A good many physical chemists now accept the probability of orientation on an inert surface, owing to the affinity of certain groups for the water of the liquid phase; for example, in the case of a fatty acid film on water, the carboxylic group has a greater affinity for the water than the terminal CH_3 groups and the molecules are regarded as arranged in parallel lines with the CH_3 group uppermost, *i.e.*, farthest away from the surface.

In the case of enzymes, all the evidence as to the very specific nature of their action is strongly in favor of some definite form of orientation—for the moment in the case of the saccharo-clasts one may imagine the hydrolyte as lying along or fitting against

the surface of the enzyme. Whether such a state of things be described as adsorption or the formation of an intermediate complex is immaterial. As Bayliss has recently pointed out, adsorption is shown only when a sufficient number of atoms are joined to form a surface. While the writer prefers to think of the forces involved as chemical, this point is largely immaterial, as the work of the Braggs has indicated that, in the case of crystals, the forces responsible for cohesion, chemical union, and electrical behavior are one and the same.

Intermediate Complexes

The conception of intermediate additive complexes is one which presents no difficulty to the organic chemist, who has used it to explain many transformations, but apparently it is not so obvious to others and it requires, therefore, a little elaboration. The chemist is acquainted with types of compounds ranging from the very stable, such as methane, to those of only transient existence breaking down into other compounds at the moment of their formation and being recognizable only by their interactions, often color changes, or by means of some more stable salt or other derivative. It should not be difficult, then, to imagine complexes which are being formed and decomposed again, the two interactions taking place with nearly the same velocity. Whereas there is only one method of forming the complex, there is, in the cases in question, more than one way of decomposing it and, in practice, it will break down in each of the possible ways, the amount of each product formed being due to other influences. For example, there is evidence that nickel, in its active state, and oleic acid form a complex in the presence of hydrogen, which, besides breaking down to nickel and oleic acid, also yields nickel and elaidic acid, the two acids being *cis-trans* isomerides, and, further, forms one or more isomeric oleic acids in which the unsaturated linkage has shifted to another position.

Such intermediate complexes can from their very nature never be isolated and characterized and their existence proved, as is demanded by some critics; otherwise they would not be sufficiently unstable to break down immediately to new products.

Enzymes as Synthetic Agents

From the theoretical point of view, enzymes, like other catalytic agents, should be capable of inducing synthetic as well as analytic changes, and it is believed that much of the synthesis in the living cell is effected by their agency. In cases where their action is least specific it has been clearly established that, in concentrated solutions of substrate, the enzyme promotes synthetic change, as, for example, lipase in the case of esters of fatty acids, and emulsin in the case of alcoholic solutions of sugars, when the corresponding alkyl-glucosides are produced up to the point of equilibrium, depending on the concentration of the sugar. In these as in others, well-authenticated experiment is in accord with theory.

Most interest attaches to the synthesis of the natural sugars and here there is much that is obscure. The synthesis of cane sugar from a mixture of glucose and fructose certainly does not take place in the presence of invertase, and the synthesis of maltose from glucose in the presence of maltase has been the subject of controversy. An explanation of the subject will probably be found in the new discoveries about the unexpected complexity of the structure of the sugars. Glucose and fructose in aqueous solution, for example, are not present in those structural forms which are believed to be the units of cane sugar and, unless the enzyme can bring them into this form, synthesis would appear to be impossible. Similarly, maltase acting on glucose in aqueous solution can only make maltose, if the right modification of glucose is available; otherwise synthesis, if effected, must result in the formation of an isomeride of maltose, for which fact there is definite experimental evidence. Thus, apparent departures from simple theory in the case of enzymes are to be attributed to the secondary cause of structural isomerism and not to any eccentricity of the enzyme.

Summary

The present state of our knowledge of enzymes may now be summarized somewhat as follows. The enzyme is an aggregate of groups in a much larger colloid complex and not an entity in the strict sense of the term. Action takes place at the surface

of the colloid and involves a momentary association between the enzyme and the substance on which it acts. The processes of purification of an enzyme involve, on the one hand, the liberation of the groups at the surface in an active form and, on the other, the elimination of all factors which are injurious to surface action, including both those which tend to dirty the surface and those which, by combining with a portion of the enzyme, render it inactive. The highly specific nature of most enzymes makes it probable that there is some relation in structure between enzyme and the substance on which it acts, as otherwise the additive complex could not be formed. In the living organism, this highly selective activity forms the mechanism regulating metabolism; without it, the downgrade changes in life would be largely uncontrolled. Once the enzyme complex is formed, an electrochemical circuit, in which active water molecules take part, is completed and, the necessary energy being supplied, in manner which has yet to be explained, the disruptive changes take place leaving the enzyme free to form a fresh complex.

REFERENCES

Armstrong, E. F. and others: Enzyme action I–XX, *Proc. Roy. Soc.* (1904) onwards, particularly **73** (1904), 500; **76** (1905), 592; **79** (1907), 360; **B, 85** (1912), 363; **B, 86** (1913), 561.

Armstrong, E. F. and Hilditch: Catalysis at solid surfaces, *Proc. Roy. Soc.*, **A, 96** (1919), 137; **A, 98** (1920), 27.

Armstrong, H. E. and Gosney: Lipase, *Proc. Roy. Soc.*, **B, 86** (1913), 586; **B, 88** (1914), 176.

Armstrong, H. E. and Horton: Urease, *Proc. Roy. Soc.*, **B, 85** (1912), 109–127; **B, 86** (1913), 328–343.

Bayliss: British Association Report on Colloid Chemistry (1918), 143.

Bourquelot and Bridel: Synthesis of glucosides with emulsin, *Ann. chim. phys.*, **28** (1913), 145.

Fischer, E.: Configuration and enzyme activity, *Ber.*, **27** (1894), 2985, 3479; **28** (1895), 1429. *Z. physiol. Chem.*, **107** (1919), 176.

Hopkins, F. G.: Oxidases, *Biochem. J.*, **15** (1921), 286; *J. Biol. Chem.*, **54** (1922), 527.

Kastle and Loevenhart: Lipase, *Am. Chem. J.*, **24** (1900), 491.

Morgan, Stewart, and Hopkins: Oxidases, *Proc. Roy. Soc.*, **B, 94** (1922), 109.

Tanaka: Lipase, *Chem. Soc. Abstr.*, (1910), i, 800.

Van Slyke and Cullen: Mode of action of urease and of enzymes in general, *J. Biol. Chem.*, **19** (1914), 141.

CHAPTER XV

JELLIES AND GELATINOUS PRECIPITATES

By

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If certain colloidal solutions of highly hydrous substances are caused to coagulate under suitable conditions, a bulky semi-solid mass is formed which is known as a jelly-like precipitate or a jelly, when there is no supernatant liquid, and as a gelatinous precipitate, when a portion of the liquid phase is visible as such. Thus, if a small amount of an electrolyte with a multivalent anion, such as potassium sulfate, is added to a colloidal solution of hydrous chromic oxide, the sol coagulates with the formation of a firm, uniform, transparent jelly which encloses all the liquid; on the other hand, if an excess of electrolyte is employed, rapid agglomeration of the colloidal particles takes place, forming a bulky, translucent, gelatinous precipitate which remains suspended in the liquid phase.[1] The chromic oxide jelly may be converted into a gelatinous precipitate by shaking, thereby partially destroying the uniform jelly structure and so permitting a portion of the enclosed liquid to escape. Jellies and gelatinous precipitates are two forms of gels. Gels of the hydrous oxides, such as chromic oxide, which lose their elasticity and become powdery on drying, are called rigid or non-elastic gels to distinguish them from elastic gels, such as gelatin and agar, which are characterized by their perfect elasticity through certain narrow limits and by retaining their elasticity and coherence on drying.

THE STRUCTURE OF GELS

Since a working theory of the structure of gels is essential for a systematic discussion of the preparation of the two types, it seems advisable to take up the question of structure first. This

[1] WEISER: *J. Phys. Chem.*, **26** (1922), 429.

question has doubtless received more attention at the hands of skilled investigators than any other single problem in the field of colloid chemistry. And it is still a very live problem, since there are such fundamental differences of opinion among eminent authorities as to the nature of a jelly. Thus Robertson, Procter,[2] and Katz[3] regard jellies as homogeneous single-phase systems, solid solutions or semi-solid solutions "of the exterior solution in the colloid in which both constituents are within the range of the molecular attractions of the mass." Wo. Ostwald[4] considers gels to be two-phase liquid-liquid systems possessing an interfacial tension, and a similar view is held by Bancroft.[5] The vast majority of investigators, however, incline to the view that jellies are two-phase solid-liquid systems, in which there is a network or cellular arrangement of solid phase permeated by liquid.

The evidence in support of the solid-solution theory of jelly structure has been drawn largely from investigations on the swelling of substances. Thus Katz, in an exhaustive monograph, points out that there is a close similarity in the phenomena associated with swelling and in the changes which accompany the formation of binary liquid mixtures. This parallelism leads to the conclusion that the swelling process is simply the formation of a solid solution between water and the swelling substance. Similarly, from a study of the system gelatin-acid-water, Procter concluded that gelatin combines with acid, forming easily dissociated salts, and that the volume of a swollen jelly under equilibrium condition is determined by the osmotic pressure of the gelatin salts and the Donnan equilibrium. While such a view may explain the swelling of gelatin, it seems inadequate to account for the change in viscosity and the loss of mobility when a warm solution of gelatin, for example, is cooled. Procter meets this difficulty by postulating the formation of tenuous and possibly flexible crystals which interlace, and possibly anastomize, when a warm molecular solution "sets" on

[2] *J. Chem. Soc.*, **105** (1914), 313.

[3] *Kolloidchem. Beihefte*, **9** (1971), 1.

[4] *Pflüger's Arch.*, **109** (1905), 277; **111** (1906), 581; "Theoretical and Applied Colloid Chemistry," translated by Fischer, 1917, p. 103.

[5] "Applied Colloid Chemistry," 1921, p. 242.

cooling. These crystals are not of microscopic dimensions and the network is, therefore, so fine that both solvent and crystals are within the range of each other's molecular forces. The solid-solution theory and the two-phase solid-liquid theory differ, therefore, in regard to the size of the particles forming the network. Since there is no reason to doubt that these particles are frequently of microscopic dimensions, the solid-solution theory cannot be of general application.

Ostwald's theory that jellies are simple emulsions of spherical or more or less distorted globules in a liquid medium meets with serious objection at the outset, since there are no emulsions known that have really the properties of jellies. The inorganic jellies certainly could not be looked upon as emulsions, particularly in those cases where a rigid crystalline structure has been detected. Recalling the applicability of Boltzmann's gas theory,[6] which considers molecules to be completely elastic material particles incapable of much deformation, and van der Waals' view,[7] that the properties of molecules must be compared with those of solids, Zsigmondy[8] assumes, as seems necessary, that the larger ultramicrons of a solid are themselves solid. The liquid properties of gels rich in water are explained by assuming that the ultramicrons are surrounded by water layers and have a certain free path and motion. Hatschek[9] has examined the emulsion hypothesis critically and finds it untenable if the assumptions necessary to allow of mathematical treatment are granted.

The assumption that jellies are solid-liquid systems is the oldest and is generally looked upon as the most satisfactory of the three general theories that have been proposed. In spite of all the work that has been done, there is, however, still a considerable difference of opinion as to the exact nature of the solid framework which is assumed to entrain the liquid phase and the manner in which this framework is formed. The earliest view was that a distensible body was porous, and that swelling resulted from water penetrating the pores and being held by capillarity or by

[6] "Vorlesungen über Gastheorie," Leipsig, 1896, p. 34.

[7] "Die Kontinuität des gasförmigen und Flüssigen Umstanden," Leipsig, 1899, p. 34.

[8] "Chemistry of Colloids," translated by Spear, 1917, p. 138.

[9] *Trans. Faraday Soc.*, **12** (1916), 17.

molecular attraction. In 1858, Nageli[10] pointed out that porous bodies and gels have such widely different properties that a theory based on their apparent similarity is untenable. As a substitute theory, he suggested that distensible bodies are made up of small anisotropic, crystal-like molecular aggregates which retain their identity even when the substance goes into (colloidal) solution. The micelles, as Nageli called them, take up water in such a manner that they are surrounded by a water layer the thickness of which is determined by the relative intensity of the attraction of the micelles for water and for each other. Jellies are thus considered to possess an interlacing or sponge structure. This conception was opposed by Bütschli[11] and by van Bemmelen,[12] who suggested that the droplets of liquid were held in a cell-like framework comparable to a honeycomb. This idea was probably suggested by the cellular structure of the stems of young plants, which enclose a relatively high percentage of water and still possess considerable rigidity. Bütschli supported his view by an extended series of observations first on foams and emulsions and later on gelatin, agar, and silicic acid jellies. He found in certain jellies a micro structure consisting of coalescing films containing water. Gelatin jellies that were homogeneous were hardened with alcohol or chromic acid in order to make their structure visible, and these likewise showed the presence of thin films. In a silica gel the films appeared to be about 0.3μ in thickness and the pockets which held the liquid from 1 to 1.5μ in diameter. Bütschli's view was supported by Quincke[13] and by Hardy,[14] but later investigations of Zsigmondy and his pupils showed that the hollows are very much finer than Bütschli's observations led him to believe. By applying the laws of capillarity to van Bemmelen's[15] results on the hydration and dehydration of silica gel, Zsigmondy[16] estimated the diameter of

[10] "Pflanzenphyslogischen Untersuchen," Zürich, 1858; "Theorie der Garung," Munich, 1879; *Cf.* FRANKENSTEIN: "Die Lehre von der Kohäsion," Breslau, 1835.

[11] "Untersuchen über Strukturen," Leipsig, 1898.

[12] *Z. anorg. Chem.*, **18** (1898), 14.

[13] *Drude's Ann.*, **9** (1902), 793, 969; **10** (1903), 478, 673.

[14] *Z. physik. Chem.*, **33** (1900), 326.

[15] "Die Absorption," 1910, p. 78.

[16] *Z. anorg. Chem.*, **71** (1911), 356.

the pores to be 0.5$\mu\mu$, that is, 200 or 300 times smaller than Bütschli observed. This was confirmed by Anderson,[17] who showed that the pores vary in size, some being as small as 10$\mu\mu$ in diameter. Working by the same method, Bachmann[18] found that gelatin jellies hardened by alcohol or chromic acid contained very much finer spaces than Bütschli supposed. Apparently, the structures observed by Bütschli, van Bemmelen, and Hardy were artifacts produced by the action of the hardening agents on the structure already existing.[19]

Hardy[20] believes that gelatin jellies consist of two phases separated by a well-defined surface; one phase, a solid solution of gelatin in water, and the other, a solution of water in gelatin. Both phases are liquid at first but with fall of temperature one becomes solid. The solid-solution phase forms on the concave side of the surface of separation when the proportion of gelatin is small, and on the convex side when the proportion of gelatin is large. In the latter case drops of liquid are held in a solid gelatin-rich phase. Bancroft[21] points out that such a jelly consists merely of a viscous medium in which liquid is dispersed and that it does not have a honeycomb structure in the sense that an emulsion has a honeycomb structure. Thompson[22] assumes that gelatin "consists of a network of solid gelatin, molecular or at least extremely fine, with pure water in the interstices." The view entertained by Bancroft differs somewhat from that of either Hardy or Thompson. The former points out that, since water peptizes gelatin under certain conditions, there is no reason why gelatin or a gelatin-rich phase should not peptize water. Accordingly, he considers that the gelatin-rich phase will always contain peptized water and the water-rich phase will always contain peptized gelatin. The separate phases will, therefore, in the nature of things, never be homogeneous.

[17] *Z. physik. Chem.*, **88** (1914), 191.

[18] *Z. anorg. Chem.*, **100** (1917), 1.

[19] *Cf.* Pauli: "Der Kolloidale Zustand und die Vorgänge in der lebendigen Substanz, Braunschweig, 1902; Fischer, A.: "Fixerung, Färbung und Bau des Protoplasms," 1899, p. 312.

[20] *Loc. cit.*

[21] "Applied Colloid Chemistry," 1921, p. 241.

[22] *J. Soc. Leather Trades' Chemists*, **3** (1919), 209.

Lloyd[23] amplifies the general view of Hardy and believes that a gelatin-jelly consists of two phases: a porous but continuous solid cellular framework, and liquid. The gelatin is assumed to exist in two chemical states: gelatin, *per se*, and gelatin in the form of soluble salts. Such jellies are systems of three components: water, gelatin, and an acid or base. On cooling a solution containing isoelectric gelatin and gelatin salts in equilibrium with free electrolytes, the insoluble isoelectric gelatin precipitates, not as crystals, but in a state of suspended crystallization forming a solid framework, which is kept extended by the osmotic pressure of the soluble gelatin salts in solution. In support of this hypothesis, isoelectric gelatin and water in the absence of so-called gelatin salts in solution were found to form an unstable clot that contracted and squeezed out liquid. It would seem, therefore, that an electrolyte must be present to form a stable gelatin jelly in accord with the view of Jordis.[24] J. Alexander[25] suggests that what Lloyd calls "suspended crystallization" may be a manifestation of the protective or crystal-inhibiting action of a portion of the gelatin solution. This would account for the fact that a jelly formed of isoelectric gelatin and water alone is apparently unstable, in the sense that it contracts and squeezes out some of the water. On account of the slight inherent tendency of gelatin to crystallize, it is doubtful whether the alleged increase in stability of a gel in the presence of a trace of electrolyte is due to inhibition of the crystallization of the gelatin phase. It seems more probable that the presence of an ion that is adsorbed may influence the nature and size[26] of the agglomerated particles and so may have an effect on the stability. Apparently, the amount of electrolyte necessary to form a stable jelly is very slight indeed, since Field[27] prepared such a jelly from a very highly purified gelatin.

Lloyd's conception of the process of gelation is criticized by Sheppard and Elliott[28] on the ground that if the isoelectric gelatin forms a rigid solid framework, there is no need of postulat-

[23] *Biochem. J.*, **14** (1920), 165.
[24] *Z. Elektrochem.*, **8** (1902), 677.
[25] "Glue and Gelatin," 1923, p. 71.
[26] Weiser: *J. Phys. Chem.*, **21** (1917), 314.
[27] *J. Am. Chem. Soc.*, **43** (1921), 667.
[28] *J. Am. Chem. Soc.*, **44** (1922), 373.

ing the existence of osmotic pressure to keep the jelly extended. Sheppard and Elliott[29] believe that any structure in a gelatin jelly is not inherent in the gelatin, but that the structure elements are resultants of physico-chemical changes of environment, not native to gelatin. Following up Meunier's[30] view, they postulate a supermolecular rather than a submicroscopic structure for gelatin. According to this view, pluri-molecular units, the smallest of which are the micelles, are built up by the "orientation of definite atomic groups entirely in the sense of the theory of molecular orientation due to structure, proposed for surface and interfacial tension phenomena by W. B. Hardy,[31] W. Harkins,[32] and J. Langmuir."[33]

The earliest investigations with the ultramicroscope on gelatin and semi-liquid hydrosols led Zsigmondy to conclude with Nageli that the structure is granular or flocculent, a view that is supported by the fact that jellies can be formed from freely moving ultramicrons.[34] Later, Zsigmondy and Bachmann[35] pointed out that, in addition to the apparently grainy structure met with in diluted gels of gelatin, agar, and silica, there is also a fibrillar structure. These fibrils or threads are sharply defined in soap jellies studied by Bachmann and later by McBain and his co-workers[36] and in barium malonate jellies studied by Flade.[37] The latter noted that the fibrils were of a crystalline character and suggested that jellies in general probably consisted of a network of crystalline threads. Stubel[38] and Howell[39] concur in this view, the latter introducing the term "crystalline gel." Gortner[40] prepared a jelly of dibenzoyl-*l*-cystine, which was found to con-

[29] *Cf.* Sheppard: *Nature*, **107** (1921), 73.
[30] *Chimie & industrie*, **6** (1920), 220.
[31] *Proc. Roy. Soc.*, **81 A** (1912), 610.
[32] *J. Am. Chem. Soc.*, **39** (1917), 354, 541.
[33] *Ibid.*, **38** (1916), 2221.
[34] Bachmann: *Z. anorg. Chem.*, **25** (1911), 125.
[35] *Kolloid-Z.*, **11** (1912), 150.
[36] Laing and McBain: *J. Chem. Soc.*, **117** (1920), 1506; Drake, McBain and Salomon: *Proc. Roy. Soc.*, London, **98 A** (1921), 395.
[37] *Z. anorg. Chem.*, **82** (1913), 173.
[38] *Pflüger's Archiv.*, **156** (1914), 361.
[39] *Am. J. Phys.*, **40** (1916), 526.
[40] *J. Am. Chem. Soc.*, **43** (1921), 2199.

sist of minute crystalline needle-like fibrils. Bradford[41] champions the theory that the reversible sol-gel transformation is merely an extreme case of crystallization. Ultramicroscopic examination of a gelatin jelly reveals the presence of spherites, which Bradford believes are made up of crystalline particles. Moeller[42] likewise believes that gelatinization is a kind of crystallization in which there is formed a lattice of crystal threads which entrains the liquid; and von Weimarn[43] concludes from his investigations that a jelly is a sponge composed of highly disperse, crystalline granules soaked in dispersive medium.

While Bradford, Moeller, and von Weimarn may have sufficient evidence to convince them that all jellies are made up ultimately of crystals, it is difficult to accept the view that there is no such thing as an amorphous precipitate of the flocculent, gelatinous, or jelly-like type. The theory that jelly formation is merely a process of crystallization seems to be contradicted by the work of Bogue, McBain, and Barratt, although all of the latter are strong supporters of a filamentous structure. Bogue[44] believes that the elastic jellies such as gelatin are made up of streptococcal threads of molecules:

> The sol consists of slightly hydrated or swollen molecules united into short chains. When the temperature falls, the threads increase in length and number and their power of water absorption increases, resulting in an increase in viscosity. A solid jelly results when the relative volume occupied by the swollen molecular threads has become so great that freedom of motion is lost and the adjacent heavily swollen aggregates cohere. The rigidity is dependent on the relative amount of free solvent in the interstices of the aggregates and on the amount of solvent that has been taken up by the gelatin in a hydrated or imbibed condition. The resiliency or elasticity is dependent upon the length and number of the catenary threads. Solution is the reverse of gelation. Swelling is determined by osmotic forces and the Donnan equilibrium.

While in certain cases the colloidal particles—the molecular aggregates, or micelles—may possess the thread-like characteristic essential for forming an entangling mesh in which each particle

[41] *Biochem. J.*, **12** (1918), 351; **14** (1920), 474.
[42] *Kolloid-Z.*, **23** (1918), 11.
[43] *J. Russ. Phys. Chem. Soc.*, **47** (1915), 2163.
[44] *Chem. Met. Eng.*, **23** (1920), 61; *J. Am. Chem. Soc.*, **44** (1922), 1343.

is discrete, in other cases it is probable that the micelles actually become stuck together or oriented into loose aggregates which may take the form of chance granules, threads, or chains. Such a linking together of the particles to form an enmeshing network seems essential in some of the extremely dilute inorganic jellies which will be referred to later on. Laing and McBain consider the gelatinization of soap to result from the linking up of colloidal particles to form a filamentous structure. "The colloidal particles in soap and gel are the same; but, whereas in the former they are independent, in a fully formed gel they become linked up probably to form a filamentous structure." The formation of the soap curd is looked upon as a phenomenon analogous to crystallization, which is distinct from the process of jelly formation. The conception of micellar orientation in the process of gelation is supported by a number of observations mentioned by Laing and McBain among which are the following: The identity in sol and gel of the electrical conductivity,[45] and the lowering of the vapor pressure; the intensifying of the molecular movement by heat, which overcomes the forces holding the particles and causes melting of the gel; the transformation of a jelly (nitrocotton) into a sol by mechanical stirring, which breaks down the orienting bonds betwen the particles;[46] the absence of Brownian movement in soap or gelatin jellies;[47] the dependence of the apparent viscosity of sols on their previous treatment and history, which influences, the degree of orientation of their particles;[48] and the frequent occurrence of supersaturation and hysteresis with regard to gelation. To these should be added the observation of Walpole[49] that the refractive index of a gelatin water system is a linear function of the concentration, and, when plotted against the temperature, no break occurs at the point of gelation; and the findings of Bogue[50] that the viscosity-plasticity change in the sol-gel transformation is gradual and regular.

[45] *Cf.* ARRHENIUS: *Öefvers. Stockholm Akad.*, **6** (1887), 121.
[46] *Cf.* ALEXANDER: "Glue and Gelatin," 1923, p. 75.
[47] BACHMANN: *Z. anorg. Chem.*, **73** (1912), 125.
[48] *Cf.* HATSCHEK: *Kolloid-Z.*, **13** (1913), 881.
[49] *Kolloid-Z.*, **13** (1913), 241.
[50] *J. Am. Chem. Soc.*, **44** (1922), 1313.

Barratt[51] observed a distinct fibrillary structure in fibrin jellies but found that they did not possess the physical character of crystals. Like Laing and McBain, he is of the opinion that the fibrils form a network structure. When a jelly was first formed by gelatinization of a fibrinogen sol, no fibrils could be detected, but later they became visible in the ultramicroscope. This led to the conclusion that the jelly was made up of fibrils that were submicroscopic at first and later ultramicroscopic. This growth of particles in jellies has been observed frequently and in some cases is unquestionably due to growth of crystals, notably with barium malonate and some of the arsenate jellies[52] and with the dyes, benzopurpurine and chrysophenene;[53] but in other cases it is the result of the agglomeration of amorphous particles. In accord with this view, Scherrer[54] showed that certain rigid jellies, like silicic acid and stannic acid, showed well-defined crystalline interference figures as well as the characteristics of amorphous bodies, whereas gelatin jellies showed no signs of a crystalline structure. Harrison[55] obtained spherical coagulation forms of starch which resembled Bradford's spherites; but he does not regard them as crystalline. As already stated, Zsigmondy and Bachmann observed ultramicroscopically the formation of jellies of gelatin, agar, and silica by agglomeration into flaky groups of freely movable ultramicrons of unknown structure. It is thus implied that all jellies are not necessarily filamentous in structure. This is supported by recent ultramicroscopic observations carried out by Harrison[56] on gelatin and cellulose jellies, which were found to consist of minute portions joined together in a somewhat irregular manner. Alexander[57] believes that the polar nature of molecules may tend to produce some kind of orientation and that some chain-like structures may be formed, but that the formation of chains or threads is not an essential of jelly formation.

[51] *Biochem. J.*, **14** (1920), 189.

[52] Diesz: *Kolloid-Z.*, **14** (1914), 139.

[53] Harrison: "The Physics and Chemistry of Colloids and Their Bearing on Industrial Questions," Report of a General Discussion held jointly by the Faraday Society and Physical Societies of London, Oct. 25, 1920, p 57.

[54] *Nach. Ges. Wiss.*, Gottingen, 1918.

[55] *J. Soc. Dyers, Colorists*, **32** (1916), 32.

[56] *Loc. cit.*, Ref. No. 53, p. 57.

[57] "Glue and Gelatin," 1923, p. 84.

He admits, however, that polar groupings in chains probably takes place to a considerable extent in dilute solutions of gelatin.

It would be highly interesting indeed if jellies of widely different substances were all essentially identical in structure. Such a condition seems altogether unlikely, but investigators have apparently sought to establish such an identity. Studies on specific jellies have led some to conclude that all jellies are made up of a framework of amorphous threads, others that they are composed of crystalline threads, and still others who fail to find any threads or filaments at all but observe an irregular grouping of particles. Doubtless all are right in specific cases. Indeed, it is not unlikely that there are various arrangements of molecular aggregates in different jellies and, perhaps, in the same jelly. In a heterogeneous mixture of complex groups, such as are found in gelatin sol or jelly, it is probable that the process of gelation and the jelly structure are more complex than in the inorganic jellies or in soap jellies. The orientation of the particles may result in fibrils in certain cases and in more or less irregular arrangements in others. In certain cases the fibrils may consist of definite crystals, while in others the crystalline characteristics may be entirely lacking. In all cases it seems probable that the particles are highly hydrous as a result of adsorption or absorption and that they are linked together, forming an irregular mesh or network in the interstices of which liquid is entrained.

Since the only essential difference between a jelly and a gelatinous precipitate appears to be that in the latter case contraction has taken place with the excretion of liquid, it is generally conceded that the two types of gels are similar in structure. While the usual gelatinous precipitates, such as hydrous chromic oxide and hydrous ferric oxide, are pretty generally considered to be amorphous, von Weimarn believes them to be made up of myriads of tiny crystals. It is apparently possible to have gelatinous crystals. Thus, Harrison[58] speaks of aqueous solutions of benzopurpurine and chrysophenene setting to jellies containing gelatinous crystals, some of them so fine that they can pass unbroken through a filter paper. Similarly, cholic acid gives a blue precipitate with iodine, which forms in clusters of needle crystals which are rigid. Under other conditions needle-

[58] *Loc. cit.*, Ref. No. 53, p. 58.

shaped crystals are formed which are gelatinous and can be bent in all shapes by moving the cover glass on the microscope slide. Some of these so-called gelatinous crystals show remarkable vibrations due to the impact of the molecules. Harrison's observations seem to throw some light on the problem of what constitutes a gelatinous crystal or aggregate, and hence on the related problem of what is a gelatinous precipitate.

Le Chatelier[59] succeeded in polishing metal with colloidal silicic acid and hence concluded that the gelatinous precipitate consists of anhydrous silica and water. Bancroft[60] considers this evidence inconclusive, since anhydrous silica may have been formed as a result of pressure during polishing, and suggests that a better method of attack is to consider whether grains of sand mixed with water will give a gelatinous precipitate. Since this does not happen, Bancroft concludes:

> We must, therefore, assume one of two things. Either the sand grains are held together extraordinarily firmly by water when they are very fine, or some other factor comes in. The first explanation cannot be the right one, because, if it were, one ought then to be able to get a gelatinous precipitate of any colloid at ordinary temperatures without much difficulty, which is not the case. We never get gelatinous gold and, while we can get gelatinous calcium carbonate, we have to do it in a very special way. Consequently, Le Chatelier's hypothesis cannot be accepted without modification.

Bancroft cites evidence to support the hypothesis that a gelatinous precipitate is a two-phase liquid-liquid system, the physical properties of which are determined by the viscous character of one of the phases. This view seems unsatisfactory and in certain cases at least is untenable. It is suggested further that solid particles and water may behave like a gelatinous precipitate when the solid particles are sufficiently fine and provided they adsorb water sufficiently strongly. As previously noted, Zsigmondy[61] explains the liquid character of gels rich in water by assuming that the ultramicrons are surrounded by water layers and have a certain free path and motion. Bancroft objects to this view on the ground that Zsigmondy does not show why it should be so. Harrison's observations on gelatinous crystals

[59] "La Silice et Les Silicates," 1914, p. 76.

[60] "Applied Colloid Chemistry," 1921, p. 236.

[61] "Chemistry of Colloids," translated by Spear, 1917, p. 138.

bear on this point. Gelatinous crystals are apparently extremely fine needle-shaped masses, so thin that they lack rigidity and so flexible that they can be bent and twisted into various shapes and may move under the bombardment of water molecules like the spiral bacteria present on the teeth. A cluster or network of such needle-shaped flexible crystals which adsorb water strongly would form a viscous or plastic mass which is usually known as a gelatinous precipitate. If the crystals are compact and rigid rather than thin and flexible, they would not form a gelatinous precipitate unless they united into threads or strings that would possess the flexibility and elasticity which characterize a thin needle crystal. Obviously, the particles need not be crystalline and, as a rule, they probably are not. A gelatinous precipitate is apparently a network composed of extremely finely divided particles which have coalesced to form flexible filaments or chains, and which adsorb water strongly, and so are highly hydrous. Where the particles do not adsorb water particularly strongly and where the tendency to coalesce into filaments or threads is not great, a high concentration of the finely divided particles is necessary, as in the case of calcium carbonate and barium sulfate. It is probable that neither tendency is very marked in the case of gold, which accounts for the fact that no one has prepared a gold jelly. However, the writer is not aware that anyone has attempted to precipitate a fairly large amount of gold in a small volume, as von Weimarn does with barium sulfate. While a gelatinous precipitate of gold has not yet been prepared, this might be a fairly simple process if some liquid other than water were employed. Börjeson,[62] working in Svedberg's laboratory, has prepared a cadmium jelly by allowing a very dilute sol of cadmium in alcohol to stand for some time in a glass bottle. In this case the particles were only 5$\mu\mu$ in radius and the concentration but 0.2 to 0.5 per cent.

Formation of Gels

If we start out with the assumption that a jelly consists of myriads of hydrous particles that have become enmeshed into a network that entrains liquids, it follows that any substance

[62] *Loc. cit.*, Ref. No. 53, p. 55.

should form a jelly, provided a suitable amount of a highly dispersed substance is precipitated and provided the particles adsorb the dispersing medium very strongly. The amount of the dispersed phase that must be present to form a firm jelly by a precipitation method will depend on the size and arrangement of the particles and the extent to which they adsorb the dispersing liquid. The methods of procedure which have been employed will be considered separately.

Formation of Jelly by Cooling Sol.—Certain substances, such as gelatin and agar-agar, swell in water at ordinary temperatures but are not peptized, forming a sol until the temperature is raised. On cooling such a sol a jelly is formed, provided the concentration is suitable. Thus, a sol containing 1 per cent of pure gelatin does not gel until around 10° and gelation does not take place at any concentration above $\pm 35°$. Bachmann[63] observed that pure, warm solutions of gelatin are almost homogeneous but that, on cooling, a new phase appears, as evidenced by a heterogeneity which is amicroscopic or submicroscopic, depending on the concentration. This process is similar in certain respects to crystallization but differs from it in that microns, submicrons, ultramicrons, and amicrons are formed, according to the concentration. The appearance of visible particles is not dependent on the formation of a jelly, as these may be seen before the jelly sets, and in dilute solutions that do not set. When a jelly results on cooling a sol, the process apparently consists in the formation of highly hydrous molecular aggregates which are linked together to form a more or less rigid network. Bogue believes that the aggregates not only grow but become more hydrous on cooling. This might be expected in view of the fact that, in general, adsorption increases rapidly with falling temperature. The sol-gel transformation in a given system does not occur at a definite transition point, but the transition is continuous and reversible over a somewhat indefinite period.[64]

Formation of Concentrated Jellies.—Many difficultly soluble salts which ordinarily precipitate in relatively large crystals can be thrown out in the form of a jelly or gelatinous precipitate from very concentrated solutions. This phenomenon was observed by

[63] *Z. anorg. Chem.*, **73** (1911), 125.

[64] Bogue: *J. Am. Chem. Soc.*, **44** (1922), 1313.

Harting,[65] Buchner,[66] Biederman,[67] Neuberg,[68] and particularly by von Weimarn.[69] The latter[70] made a systematic study of the form in which substances precipitate from solution. He calls attention to the fact that precipitation depends on a number of very different factors; on the solubility of the substance; on the latent heat of precipitation; on the concentration at which the precipitation takes place; on the normal pressure at the surface of the solvent; and on the molecular weights of the solvent and the solute. He points out the impossibility of taking all of these factors into account and simplifies the problem by considering first but two of the factors, the solubility of the precipitating substance and the concentration at which precipitation begins. The effect of viscosity is discussed briefly in a later work.[71] The process of condensation (precipitation) is divided into two parts: the first stage, in which the molecules condense to invisible or ultramicroscopic crystals; and the second, which is concerned with the growth of the particles as a result of diffusion. The velocity at the important first moment of the first stage of the precipitation is formulated thus:

$$W = K\frac{\text{Condensation pressure}}{\text{Condensation resistance}} = K\frac{Q - L}{L} = K\frac{P}{L} = KU$$

where W is the initial rate of precipitation, Q the total concentration of the substance which is to precipitate, L the solubility of coarse crystals of the substance, $Q - L = P$ the amount of supersaturation. The ratio $\frac{P}{L} = U$ is the percentage supersaturation at the moment precipitation begins.

The velocity of the second stage is given by the Nernst-Noyes equation:

$$V = \frac{D}{S} \cdot O \cdot (C - l)$$

[65] "Recherches de morphologie synthétique sur la production artificielle de quelques formations calcaries organiques," Amsterdam, 1872.

[66] *Chem. Ztg.*, **17** (1893), 878.

[67] *Z. allgem. Physiol.*, **1** (1902), 154.

[68] *Sitzb. Akad. Wiss.*, Berlin, 1907, 820.

[69] "Zur Lehre von den Zuständen der Materie," 1914.

[70] Von Weimarn: "Grundzüge der Dispersoidchemie," (1911) p. 30.

[71] "Zur Lehre von den Zuständen der Materie," (1914) p. 21; *Kolloidchem. Beihefte*, **4** (1912), 101.

where D is the diffusion coefficient, S the thickness of the adherent film, O the surface, C the concentration of the surrounding solution, and l the solubility of the dispersed phase for a given degree of dispersity. $C-l$ may be termed the absolute supersaturation.

From these general formulations, von Weimarn arrives at the conclusion that jellies are obtained only when the ratio $\frac{P}{L}$, that is, the percentage supersaturation U, can be made enormous. It is pointed out that the nature of a precipitate is quite different, depending on whether a given value of U is obtained by a large P or by a small L. If a large U is obtained by a high value of P, a large amount of disperse phase is produced and a gel forms, while if P is small and L very small, a relatively small amount of disperse phase is produced and a sol is formed. Von Weimarn has demonstrated the accuracy of his deductions in a large number of cases, using reacting solutions of high concentrations; and it is apparently true that any salt can be obtained in a gelatinous form if the concentration of the reacting solutions, and so the velocity of precipitation, is sufficiently high. Thus von Weimarn[72] prepared jellies of substances like $BaSO_4$, which usually precipitates in the form of crystals, by mixing very concentrated (3 to 7 N) solutions of manganese sulfate and barium thiocyanate. This is not the condition under which jellies are usually obtained, and their existence is temporary. By mixing very high concentrations of materials which react to form an insoluble precipitate, a very large number of relatively small particles is formed because of the high degree of supersaturation.[73] Each of these minute particles adsorbs a little water and, as they are very close together, a semi-solid mass results, which entrains all the liquid phase, thus forming what has been termed a jelly. These so-called jellies break down on standing, on account of growth of the particles and the consequent liberation of adsorbed water. Precipitates in which the ratio of mols of water to mols of salt is, say, 20:1 or 25:1 should not be considered as jellies in the same sense as precipitates in which this ratio is two or three hundred times as great. Very finely divided sand or fuller's earth may be matted in the bottom of a test tube and this

[72] "Zur Lehre von den Zuständen der Materie," (1914), p. 21.

[73] BANCROFT: *J. Phys. Chem.*, **24** (1920), 100.

solid will take up a great deal of water before a supernatant water layer is observed; but such a preparation should not be called a jelly. It seems that von Weimarn's barium sulfate jelly may be similar, except that the particles are much smaller, and so a given amount will take up more water. On the other hand, with true jellies, where the amount of enclosed water may be relatively enormous, time must be allowed for the formation of a definite structure. As a matter of fact, von Weimarn[74] recognized a difference between a $BaSO_4$ jelly prepared by his method and a jelly formed by uniform gelatinization of a liquid throughout its mass, as in the case of gelatin jelly. The former he terms a "coarsely cellular gel" and the latter a "reticulated gel."

Formation of Jellies by Precipitation from Sol.—Since finely divided particles which adsorb water strongly are of primary importance for the formation of a hydrous jelly, it would seem that the most promising method of preparing dilute jellies would be to precipitate hydrous substances from colloidal solution. The von Weimarn theory would tell us, of course, that this precipitation would have to take place at a suitable rate under conditions that are not conducive to growth of the individual particles, but it does not enable us to predict the optimum rate of coagulation, the effect of salts on jelly formation, or the conditions which determine the formation of a jelly rather than a gelatinous precipitate. As a result of recent investigations on the formation of typical dilute inorganic jellies, the writer has outlined the general conditions of jelly formation and the effect on the process of various factors other than the percentage supersaturation "at the important first moment of the first stage of condensation" from molecules to invisible crystals. Jellies would be expected to form from colloidal solution if a suitable amount is precipitated at a suitable rate without agitation in the absence of a medium that exerts an appreciable solvent or peptizing action. If the concentration of the colloid is too low, no jelly, or only a very soft jelly, can result. If the velocity of precipitation is too great, contraction is likely to occur, with the formation of a gelatinous precipitate instead of a jelly. The effect of the presence of salts on jelly formation is, therefore, determined, in large measure, by the precipitating and stabilizing

[74] *J. Russ. Phys. Chem. Soc.*, **47** (1915), 2163.

action of the ions in so far as these affect the rate of precipitation. In general, a slow rate of precipitation is to be preferred if there is little or no tendency of the particles to grow as a result of the solvent action of the electrolyte. The favorable concentration for different electrolytes is in the immediate region of their precipitation concentration. A little below this value no precipitation, or only a slight precipitation, takes place, while above this value coagulation is usually so rapid that a gelatinous precipitate is formed instead of a jelly. The reason is that time is not allowed for the uniform mixing of the colloid with coagulant, and the slow uniform precipitation necessary for the building of a uniform jelly structure is replaced by rapid uneven coagulation and the consequent contraction which distinguishes a gelatinous precipitate from a jelly.

The accuracy of these deductions has been demonstrated repeatedly in the writer's laboratory using sols of the hydrous oxides of chromium[75] (both positive and negative), tin,[76] copper,[77] aluminum, and the arsenates of iron and aluminum.[78] In many cases these jellies may be obtained in relatively low concentration. A notable example is the case of chromic oxide, which formed a firm jelly containing but 0.18 per cent Cr_2O_3 and a soft jelly containing 0.09 per cent Cr_2O_3. Firm jellies of such low concentrations are comparatively rare, though Döehle and Rassow[79] obtained jellies of the mercury salt of an organic sulfo acid in concentrations of 0.72 per cent, while Foerster found that camphorylphenylthiosemicarbazide formed stiff jellies in concentrations of 0.33 per cent and trembling jellies in concentrations of 0.25 per cent.[80] Attention has already been called to Börjeson's cadmium jelly and to Gortner's dibenzoyl-*l*-cystine jelly, both of which could be prepared in concentrations as low as 0.20 per cent. The formation of such dilute jellies results only when the particles are very hydrous and when the conditions of precipitation allow time for the building up of an enmeshing

[75] Weiser: *J. Phys. Chem.*, **26** (1922), 419, 424.
[76] *Ibid.*, **26** (1922), 689.
[77] *Ibid.*, **27** (1923), 685.
[78] *Ibid.*, **28** (1924), 1.
[79] *Kolloid-Z.*, **12** (1913), 71.
[80] Hatschek: *Ibid.*, **11** (1912), 158.

network. In case the particles are but slightly hydrous and show but little tendency to link together into threads, extremely high concentrations must be present, as von Weimarn found. Unfortunately, there has been no systematic work done on the formation of jellies from non-aqueous sols.

Formation of Jellies by Dialysis of Sol.—On dialysis of a colloidal solution of ferric arsenate peptized by ferric chloride, Grimaux[81] obtained a firm, transparent jelly. This observation has been confirmed and extended by Holmes and his pupils.[82] Similar observations have been made in the writer's laboratory with hydrous chromic oxide, and the method is probably a general one. From the point of view outlined in the foregoing section, the formation of jellies by dialysis of a colloidal hydrous substance is readily understood. Dialysis merely removes the stabilizing ion slowly and uniformly below the critical value necessary for peptization, and precipitation results just as if the adsorption of the stabilizing ion were compensated for or neutralized by the addition of an electrolyte having a suitable precipitating ion. The accuracy of these deductions has been demonstrated conclusively in a series of investigations on the arsenates of iron and aluminum.[83]

Formation of Dilute Jellies by Metathesis.—The von Weimarn theory tells us that mixing dilute solutions which interact at once will not give a jelly, since the percentage supersaturation $\frac{P}{L} = U$ is too small because of the small value of P. As a matter of fact, however, jellies have been obtained under certain conditions by mixing very dilute solutions, in which L is sufficiently large that precipitation is slow and quantitative precipitation impossible, so that $\frac{P}{L} = U$ is small. Such cases are apparently not covered by the von Weimarn theory. It is quite possible to obtain a gelatinous precipitate by mixing dilute solutions of two salts which precipitate immediately (P small,

[81] *Compt. rend.*, **98** (1884), 1540.

[82] Holmes and Rindfusz: *J. Am. Chem. Soc.*, **38** (1916), 1970; Holmes and Arnold: *Ibid.*, **40** (1918), 1014; Holmes and Fall: *Ibid.*, **41** (1919), 763.

[83] Weiser: *J. Phys. Chem.*, **28** (1924), 26.

but L very small), but a jelly will not form under these conditions. The reason is evident when we consider the impossibility of obtaining the instantaneous mixing of the solutions which is essential for uniform precipitation throughout the solution. One part is precipitated before another is mixed with the precipitant, and the uniformity which is characteristic of a jelly is lost. Moreover, the mixing itself will tend to destroy the jelly structure. The results are, therefore, not unlike those obtained when a colloid capable of forming a jelly by slow precipitation is coagulated too rapidly by the addition of excess electrolyte. To obtain a jelly from a colloidal solution, it is necessary to add such an amount of electrolyte that thorough mixing is possible before appreciable coagulation takes place. From these considerations it follows that precipitation of a hydrous substance as a result of double decomposition might form a jelly instead of a gelatinous precipitate, in case the thorough mixing of the solutions could be effected before precipitation began, and in case the precipitation once started, proceeded at a suitable rate. Such conditions do not obtain as a rule, but they are quite possible theoretically. Thus, the precipitation may be the result of a stepwise process, one step of which proceeds at a suitably slow rate. It is further possible to have a reaction which proceeds very slowly at low temperatures but with marked velocity at higher temperatures. This would not only allow of mixing without precipitation but would enable one to control the subsequent rate of reaction by a suitable regulation of the temperature.

Such a favorable combination of circumstances apparently obtains when a manganese salt of a strong acid and KH_2AsO_4 are mixed. The latter salt ionizes thus: $KH_2AsO_4 \rightleftarrows K^+ + H_2AsO_4^-$; but, on account of the solubility of $Mn(H_2AsO_4)$, no Mn^{++} ions are removed from solution by interaction with $H_2AsO_4^-$. The latter ion undergoes secondary ionization to a slight degree, however, as follows: $H_2AsO_4^- \rightleftarrows H^+ + HAsO_4^-$; and insoluble $MnHAsO_4$ is formed in accord wth the reaction: $Mn^{++} + HAsO_4^- = MnHAsO_4$.[84]

Since the precipitation of $MnHAsO_4$ is accompanied by the formation of an equivalent amount of free hydrogen ion in solution, an equilibrium is set up which prevents the complete pre-

[84] DIESZ.: *Kolloid-Z.*, **14** (1914), 139.

cipitation of the manganese. The amount of $MnHAsO_4$ formed and the rate of formation by the above process, however, are apparently influenced to a marked degree by the temperature, so that it should be possible to obtain good jellies by mixing dilute solutions of the necessary salts in the cold and allowing the mixture to stand at room temperature or warming to a suitable temperature. This was demonstrated with the arsenates of manganese, cobalt, iron, cadmium, and zinc.[85] When the precipitated particles are very highly hydrous, and when the tendency to crystallize is slight, very dilute jellies may be prepared by this method. Thus, a firm jelly was formed with 0.5 per cent, and a soft jelly with but 0.25 per cent, $MnHAsO_4$. On the other hand, where there is a marked tendency to crystallize, a permanent jelly cannot be obtained, as in the case of cadmium arsenate. If the conditions were altered so as to bring about very rapid precipitation, a gelatinous precipitate instead of a jelly was thrown down. Flade[86] has examined the manganese arsenate jelly microscopically and has found it to consist of fibrils or filaments like the barium malonate jellies. Here again the time factor is important for the formation of an enmeshing network of hydrous filaments.

Swelling.—Practically all substances which form the so-called elastic gels show the capacity of swelling in a suitable liquid. Thus, dry gelatin, fibrin, and starch will swell in water at ordinary temperatures, forming jellies that are peptized at higher temperatures, forming sols. Similarly, albumin swells in water but not in alcohol, benzol, ether, or turpentine. Vulcanized india rubber swells in various organic solvents, such as benzol, toluol, and xylol, but not in water; and soaps swell in water and in many organic solvents. Numerous theories[87] have been advanced to explain the phenomenon, but there is as yet no explanation that suffices to account for the fact that certain substances swell in only a limited number of liquids. The swelling of gelatin has been studied most extensively and has been found to depend on a number of factors, among which may be mentioned the

[85] Weiser: *J. Phys. Chem.*, **28** (1924), 26.

[86] Note in *Kolloid-Z.*, **14** (1914), 141.

[87] These theories have been summarized and their limitations pointed out in a paper by Bartell and Sims: *J. Am. Chem. Soc.*, **44** (1922), 289.

hydrogen ion concentration,[88] the addition of neutral salts,[89] the temperature, and the structure.[90] The importance of the hydrogen ion concentration on the swelling phenomenon was suggested by Ostwald and has been emphasized particularly by Procter and by Loeb. Fischer believes that the effect of acids is not the same at the same hydrogen ion concentration on account of the influence of the anion of the acid, which varies as indicated by the well-known lyotrope or Hofmeister series. Loeb found that only the anions of neutral salts were taken up by gelatin on the acid side of the isoelectric point (pH 4.7) and only cations on the alkaline side, whereas both ions of a neutral salt would be expected to have an effect in accord with the Hofmeister series. As a matter of fact, Loeb was working with very low concentrations of salts, and so detected no effect of cations other than hydrogen on the acid side and of anions other than hydroxyl on the basic side. At higher concentration of neutral salts the specific effect of ions other than hydrogen and hydroxyl would doubtless appear. This inference is supported by work carried out in the writer's laboratory on the adsorption of anions by hydrous chromic oxide on the alkaline side of the isoelectric point. If the concentration of the anion under consideration is very large relatively to that of hydroxyl, the effect of the latter is negligible, whereas if the hydroxyl ion concentration is appreciable, the adsorption of the other ion is cut down enormously and may be completely nullified.

As previously noted, Procter and Loeb champion the theory that gelatin forms readily soluble and highly ionized salts, such as gelatin chloride and sodium gelatinate, and that the osmotic pressure of these salts and the Donnan equilibrium determine the swelling of a gelatin jelly. While this theory may explain adequately the swelling phenomena of gelatin, it is apparently inapplicable to such cases as the swelling of rubber in benzol or

[88] Chiari: *Biochem. Z.*, **38** (1911), 167; Procter: *J. Chem. Soc.*, **105** (1914), 313; Loeb: *J. Gen. Physiol.*, **1** (1918), 41.

[89] Hofmeister: *Archiv. experim. Pathol.*, **27** (1890), 395; **28** (1891), 210; Pauli: *Pflüger's Archiv.*, **67** (1897), 219; **71** (1898), 333; Spiro: *Beitrage Chem. Physiol.*, **5** (1904), 276; Ostwald: *Pflüger's Archiv.*, **108** (1905), 563; Fischer: "Edema," New York, 1910.

[90] Procter and Burton: *J. Soc. Chem. Ind.*, **35** (1916), 404; Arisz: *Kolloidchem. Beihefte*, **7** (1915), 49.

xylol, where the existence of a Donnan equilibrium is precluded by the absence of dissociation.[91]

The previous history of a piece of dry gelatin seems to have a very marked effect on its capacity to absorb water and swell. Thus, Arisz prepared a 20 per cent jelly which was allowed to swell to a 10 per cent jelly. The 10 per cent jelly prepared in this way would not take up as much additional water in a reasonable time as a jelly made up at 10 per cent directly. Bancroft reports that Cartledge prepared 8, 16, 24, and 32 per cent gelatin jellies which were dried at room temperature to a concentration of about 96 per cent. When placed in water, each swelled rapidly to the original concentration and then took up water but slowly. B. Humiston made similar observations under the writer's direction at the Catholic University branch of the American University Experiment Station during the war. These observations indicate that the structure of gelatin may have a marked influence on its capacity to swell, a possibility which will have to be taken into account in any theory of the swelling process.

As noted above, the dehydration and swelling of a gelatin jelly is reversible over a considerable range. This is not the case with a silicic acid jelly. Van Bemmelen[92] showed that a silica gel containing a great deal of water shrinks very much when the water is removed; and, while it will take up some water again, the volume change is not reversible. If the drying is carried sufficiently far, pores are developed which are filled with air, and these pores can then be filled with a liquid other than water; but there is no appreciable swelling. When gelatin is dried, such pores are not developed and a dry gel of natural gelatin will not adsorb benzene.

Although the porous mass formed by drying a non-elastic gel will not swell in organic liquids, Graham found that such liquids will replace the water in a jelly. Thus, a silica jelly containing 11 per cent SiO_2 was suspended repeatedly in alcohol and an alcogel was formed having approximately the same volume as the original jelly. In a similar way, the water was replaced by inorganic and organic acids. Van Bemmelen substituted acetone for

[91] Fischer, M. H., in "Glue and Gelatin," by Alexander, J., p. 93.
[92] "Die Absorption," 1910.

the water, and Bachmann[93] substituted benzol. Neuhausen and Patrick[94] found that the replacement of water was not so complete as Graham reported on repeated immersions of a silica jelly in anhydrous alcohol or benzol. Elastic jellies show a similar behavior. Thus, Bütschli[95] found that it was comparatively easy to replace the water in a gelatin jelly with alcohol and this again by chloroform, turpentine, or xylol, even though dry gelatin does not swell in these liquids.

Properties of Gels

Vapor Pressure Relations.—Freshly precipitated gelatinous oxides, such as the hydrous oxides of iron, chromium, aluminum, tin, and silicon, have a vapor pressure almost the same as water and maintain it until the water content of the gels is lowered quite appreciably. Van Bemmelen[96] has examined a large number of such oxides and has found that the loss of water in dry air is continuous, the vapor pressure curve showing no breaks such as would be expected if definite chemical compounds—hydrates—were formed. Formulas for hydrates of precipitated oxides are frequently given in the literature, but in the vast majority of cases the composition indicated by these formulas is purely accidental, depending as it does on so many factors, such as the conditions of formation, the method of drying, and the age.[97] In general, it may be said that the metallic oxides precipitated in a highly gelatinous form are never hydrates, so that they should be looked upon as hydrous oxides rather than hydrous hydrated oxides. This does not mean that there are no hydrates of the metallic oxides, for there are a few, among which may be mentioned $Fe_2O_3 \cdot H_2O$ and $Al_2O_3.3H_2O$; but, as a rule, these must be prepared in a very special way.

An elastic jelly, such as gelatin, loses water continuously in dry air, just as does a gelatinous oxide;[98] but, unlike the latter,

[93] *Z. anorg. Chem.*, **73** (1912), 165.

[94] *J. Am. Chem. Soc.*, **43** (1921), 1844.

[95] "Uber den Bau quillbarer Körper," Göttingen, 1896.

[96] "Die Absorption," 1910.

[97] Weiser: *J. Phys. Chem.*, **24** (1920), 277, 505; **26** (1922), 402, 654; **27** (1923), 501.

[98] Katz: *Z. Elektrochem.*, **18** (1911), 800.

the process is very much more nearly reversible, a dry plate taking up moisture and swelling again in moist air. As already pointed out, pores are not developed by the dehydration, as in the case of silica gel. A still more striking difference between the non-elastic and elastic gels is that the former will take up a great deal more water when dipped in the liquid than when suspended in the vapor at the same temperature. Von Schröder[99] studied the behavior of gelatin in liquid water and in water vapor and was led to conclude that the vapor pressure of water in gelatin must be higher than that of pure water because water distills from the gelatin to the vapor phase. Bancroft[100] explains von Schröder's results by assuming that gelatin has a cellular structure. The walls of the cell will adsorb a certain amount of water from the saturated vapor, but the microscopic cells or pockets will not be filled unless the gelatin is immersed in water. On lifting the swollen jelly into the vapor phase, water will distill from the curved microscopic droplets to the plane surface of water in the containing vessel, because of the higher vapor pressure of the former. As Bancroft points out, the objection to this explanation is that it postulates a cellular structure for gelatin which seems more and more improbable in the light of recent investigations. Wolff and Buchner[101] claim that water does not distill from a fully distended gelatin jelly into the vapor phase and that von Schröder's conclusions are the result of experimental error. Washburn[102] found that moistened clays will dry in a closed vessel above water, a result that supports von Schröder's observations; but he believed this to be due to the action of gravity. There seems no way of settling the question except by a careful repetition of von Schröder's experiments.

Whenever a dry gel takes up moisture, heat is evolved[103] and a contraction in volume[104] takes place, particularly in the earlier stages. Although the volume of the system water + dry gel

[99] *Z. physik. Chem.*, **45** (1903), 109.

[100] "Applied Colloid Chemistry," 1921, p. 75.

[101] *Kon. Akad. Wet.*, Amsterdam, **17**, May 30 (1914); *Z. physik. Chem.*, **89** (1915), 271.

[102] *J. Am. Ceramic Soc.*, **1** (1918), 25.

[103] Wiedemann and Lüdeking: *Wied. Ann.*, **25** (1885), 145; Rodewald: *Z. physik. Chem.*, **24** (1897), 193.

[104] Lüdeking: *Wied. Ann.*, **35** (1888), 552.

is greater than that of the swollen gel, the gel itself increases in volume and so may exert a very high pressure. In some experiments on dried seaweeds, Reinke[105] found that water was taken up against a pressure of 41 atmospheres, the volume increase amounting to 16 per cent. Similarly, Rodewald[106] found that starch swells against a pressure of 2,500 atmospheres. Posnjack[107] observed the amount of water with which gelatin is in equilibrium at various pressures and on the corresponding behavior of raw rubber in different organic solvents. In all experiments the amount of liquid taken up decreases with increasing pressure. The data do not enable us to determine what pressure would be necessary to prevent any swelling or to remove all the absorbed liquid from a swollen jelly; these values would probably be very high in every case. Some idea of the magnitude of the swelling pressures of gelatin may be obtained by coating a glass plate with gelatin which has absorbed the maximum amount of water and observing the degree to which the glass plate is bent by the drying film of gelatin.[108] The strain is frequently sufficient to break the plate or to pull pieces of glass off the surface.

Elasticity.—The elasticity of gelatin gel has been investigated most extensively since it may be readily molded into any desired shape and comparable samples are fairly easily obtained. The values of the modulus of elasticity obtained by different investigators[109] agree fairly well considering the differences in method of procedure. Leick obtained values that range from 2.42 g. per mm.^{2} for a 10 per cent jelly to 29.4 for a 45 per cent jelly. The modulus was found to be roughly proportional to the square of the concentration. The value varies with the load and is not constant until after a 24-hour period of setting. Poission's ratio—the ratio of the relative contraction of the diameter to the relative change in length—has been determined repeatedly[110] for gelatin and found to be 0.5, showing that there

[105] *Hanstein's botan. Abhandl.*, **4** (1879), 1.

[106] *Z. physik. Chem.*, **24** (1897), 193.

[107] *Kolloidchem. Beihefte*, **3** (1912), 417.

[108] GRAHAM: *J. Chem. Soc.*, **17** (1864), 320.

[109] MAURER: *Wied. Ann.*, **28** (1866), 628; FRAAS: *Ibid.*, **53** (1894), 1074; LEICK: *Drude's Ann.*, **14** (1904), 139.

[110] MAURER: *Loc. cit.*; FRAAS: *Loc. cit.*; LEICK: *Loc. cit.*; BJERKEN: *Wied. Ann.*, **43** (1891), 817.

is no actual change in volume when a gel undergoes extension. The elasticity modulus of gelatin is influenced by the presence of various substances added to the gel, just as these affect gelation. Thus, Leick finds that chlorides lower the value just as they lower the viscosity and setting temperature of the sol, while glycerin and cane sugar have the opposite effect on each of the constants.

The elasticity of gelatin gels is perfect only for small loads applied for a short time; yet but little work has been done on the relaxation time in such systems. Rankine[111] maintained 3.5 to 4.5 per cent jellies at constant strain and plotted the stress necessary to do this against time. With the concentrations of jelly he employed, the stress never became zero. Reiger[112] determined the relaxation time optically by observing the disappearance of double refraction produced by strain. He found a relaxation time of 10 minutes for a 20 per cent jelly and of 41 minutes for a 40 per cent jelly at a temperature of 29°. The conditions are different at lower temperatures, as observed by Hatschek.[113] The latter bent a rectangular prism of a 10 per cent jelly and held it at 15° for 5 days until the stress disappeared and the jelly could be moved without straightening itself appreciably. Photographs taken in polarized light, when the stress was first applied, and at the end of the 5-day interval were practically identical. The optical anisotropy caused by strain did not disappear even after the external stress was removed. Similar observations were made by Harrison[114] with india rubber, cotton, wool, silk, and other fibers and by Auerbach[115] with cotton and woolen threads. Bradford[116] believes that gel substance deposits on the larger particles of a jelly on standing. If a jelly is held under a strain, the particles will be cemented in their constrained position and so cannot move on removal of the stress. The persistence of the optical appearance in polarized light is thus attributed to the internal mechanical strain.

[111] *Phil. Mag.*, **12** (1906), p. 447.
[112] *Physik. Z.*, **2** (1901), 213.
[113] *Loc. cit.*, Ref. No. 53, p. 37.
[114] *Proc. Roy. Soc.*, **A 94** (1918), 460.
[115] *Kolloid-Z.*, **32** (1923), 369.
[116] *Loc. cit.*, Ref. No. 53, p. 56.

As has been pointed out, the elasticity modulus of a gelatin jelly increases approximately as the square of the concentration and the relaxation time likewise increases rapidly with increasing concentration of gel. Since the product of elastic modulus and relaxation time is viscosity, it follows that the viscosity must show a marked increase with increasing concentration.

A gelatin jelly becomes warmer when it is stretched and cooler when compressed, just as rubber does. The compressibility[117] of gelatin is 10×10^{-6}, which is approximately ten times greater than that of solids at ordinary temperatures. The compressibility increases with rising temperature and when the jelly liquefies it becomes 48×10^{-6}, the value for water.

Non-elastic jellies may vibrate like a rigid body under certain conditions. This phenomenon has been investigated by Holmes, Nicholas, and Kauffman.[118] Some jellies were obtained in a glass test tube that gave a tone two octaves above middle C. It was demonstrated that the vibrations were not longitudinal but were transverse, the vibration frequency varying approximately inversely as the diameter of the cylinder of jelly. If the jellies were prevented from touching the walls of the glass tube by coating the latter with vaseline, the vibration frequency was much lower than for similar jellies adhering to the walls. As ordinarily prepared, the jellies are in a state of strain or tension and this affects the pitch of the tones they emit. The vibration frequency is increased by increasing the concentration of silicic acid and by the presence of excess mineral acid, factors that increase the tension and thus the effective rigidity. The same factors that increase the vibration frequency increase the syneresis of the jelly, thus showing that both vibration and syneresis have a direct relation to tension.

Optical Properties.—In the preceding section reference has been made to the double refraction produced in a jelly when subjected to mechanical deformation. This property is possessed by very dilute sols of gelatin, gum, collodion, etc., as well as by jellies. It does not occur, however, in solutions of glycerol and gelatin

[117] BARUS: *J. Am. Chem. Soc.*, **6** (1898), 285.

[118] *J. Am. Chem. Soc.*, **41** (1919), 1329; *Cf.* KOHLRAUSCH: *Z. physik. Chem.*, **12** (1893), 773; HATSCHEK: "Introduction to the Physics and Chemistry of Colloids," 1916, p. 55.

which are more viscous than the sols, and so cannot be due to ordinary viscosity. There appears to be no satisfactory explanation of the ultimate cause of the optical phenomenon but it seems reasonable to assume that the appearance of strained elastic sols and gels in polarized light is due to the effect of the stress on the elastic solid or semi-solid phase. This view seems to accord with the observations on gelatin jellies by Leick,[119] who found that the double refraction is approximately proportional to the concentration of the jelly and approximately proportional to the strain. Salts affect the double refraction in much the same way as they influence the modulus of elasticity.

The double refraction in sols and jellies subjected to strain should be distinguished from the phenomenon that frequently occurs in sols, even when no external stress is applied. Thus, Freundlich, Schuster, and Zocher[120] find that double refraction occurs on cooling down a solution of benzopurpurine. This is attributed to the development of long particles as a result of ordered coagulation, which must be differentiated from the usual unordered coagulation. Similarly, Humphrey[121] observed double refraction as a result of motion in a vanadium pentoxide sol. In this case the phenomenon is assumed to result from the formation of rod-shaped particles which set themselves in a definite direction when the liquid is caused to move.

Gelatin in solution possesses the property of mutarotation. Smith[122] has shown that the specific rotatory power of a 3 per cent commercial gelatin figured on a moisture-and-ash-free basis is $-141°$ at 35°C. and $-313°$ at 15°C. The property is attributed to a thermo-reversible equilibrium that may be represented thus: Sol from A$\rightleftarrows$gel from B. This reaction appears to be bimolecular. The increase in levorotation on lowering the temperature, which signifies increasing formation of the gel form B, closely parallels increase in viscosity. Sulfates displace the equilibrium toward the gel side between 15° and 35°, whereas chlorides, bromides, and iodides lower the viscosity and shift the equilibrium toward the sol side.

[119] *Drude's Ann.*, **14** (1904), 139.

[120] *Z. physik. Chem.*, **105** (1923), 119.

[121] *Proc. Phys. Soc.*, London, **35** (1923), 217.

[122] *J. Am. Chem. Soc.*, **41** (1919), 135; *Cf.* ALEXANDER: "Glue and Gelatin," 1923, p. 77.

The refractive index of both gelatin sols and gels has been shown by Walpole[123] to be a linear function of the gelatin concentration. As previously mentioned, the curve obtained by plotting refractive index against temperature shows no discontinuity when the sol is transformed into a jelly. This indicates that the transformation from sol to jelly is a gradual and regular process, such as would be expected if the transition was a consequence of the linking up into loose aggregates of particles already existing.

Diffusion.—The early investigations of Graham[124] led him to conclude that the rate of diffusion of salts in a gelatin jelly is the same as in pure water. But later work of Nell[125] and Bechold and Ziegler[126] showed that the resistance to diffusion is negligible only in case the gels are quite dilute, and Demanski[127] found that the conductance of a gelatin solution is always less than that of pure water. These observations are in accord with what one might expect if the structure of the jelly is an enmeshing network of hydrous particles. A thin mesh will have but little effect on the rate of diffusion of an electrolyte, whereas a thick mesh will tend to retard the process. The rate of diffusion of a sol into a jelly will be very slow indeed on account of the resistance offered by the network to the passage of particles of colloidal dimensions. Bechold[128] found that hardened gelatin could be employed for ultrafiltration, since the network structure holds back colloidal particles while allowing solutes to pass through, just as collodion filters do.

The presence of certain solutes in a jelly may have an influence on the rate of diffusion of other solutes. Thus, Bechold and Ziegler[129] found that NaCl and NaI had little effect, whereas Na_2SO_4, dextrose, glycerin, and alcohol reduced the rate of diffusion of certain solutes. There seems to be a qualitative parallelism between the effect of solutes on the elastic modulus

[123] *Kolloid-Z.*, **13** (1913), 241.
[124] *Liebig's Ann.*, **121** (1862), 5, 29.
[125] *Drude's Ann.*, **18** (1905), 323.
[126] *Z. physik. Chem.*, **56** (1906), 105.
[127] *Z. physik. Chem.*, **60** (1907), 553.
[128] *Z. physik. Chem.*, **60** (1907), 257.
[129] *Loc. cit.*

and the rate of diffusion in the sense that substances which increase the former reduce the latter.[130]

A study of chemical reactions in jellies is made possible by the ease with which electrolytes diffuse in such media. The usual method of procedure consists in adding one electrolyte to a sol, which is allowed to set, after which a solution of a second electrolyte is poured on the jelly and allowed to diffuse into the mass, where interaction takes place. If a crystalline precipitate is formed by the reaction, the crystals will be much larger and well formed than if the solutions are mixed directly. By this procedure, Hatschek and Simon[131] prepared gold crystals in a silicic acid jelly by reducing gold salts with a number of reducing agents. Hatschek[132] also prepared fairly large crystals of several insoluble salts in gelatin and silicic acid jellies. Hatschek's work has been confirmed and extended by a number of investigators, particularly by Holmes[133] who prepared magnificent crystals of several metals and salts in silicic acid jellies. The function of the jelly is to prevent rapid mixing of the interacting solutions, thus avoiding rapid precipitation and the consequent formation of amorphous particles or small crystals.

Under certain conditions, reactions in jellies carried out as described above lead to the formation of rhythmic bands of precipitates instead of large crystals. This interesting phenomenon was first noted by Liesgang,[134] who obtained rhythmic rings of silver chromate when a drop of silver nitrate was placed on a gelatin film containing dilute potassium chromate. Ostwald explained the formation of the rings in Liesgang's experiment by postulating that the silver chromate forms a supersaturated solution which diffuses along with the silver nitrate until the metastable limit is reached, when it precipitates. By repetition of the process, alternate gaps and bands are produced. Bechold[135] believes that the precipitate which constitutes the

[130] Furth and Bubanovic: *Biochem. Z.*, **90** (1918), 265; **92** (1918), 139; Stiles: *Biochem. J.*, **14** (1920), 58.

[131] *J. Soc. Chem. Ind.*, **31** (1912), 439; *Mining Eng. World*, **37** (1912), 280.

[132] *Kolloid-Z.*, **10** (1912), 77.

[133] *J. Phys. Chem.*, **21** (1917), 709.

[134] *Liesgang's phot. Archiv.* (1896), p. 321.

[135] *Z. physik. Chem.*, **52** (1905), 185.

bands is slightly soluble in the reaction products and hence that new bands can form only after a point is reached where the concentration of the reaction products is sufficiently small. Bradford[136] suggests that one of the reacting solutes is adsorbed by the growing precipitate, thus giving zones which are practically free from it. Holmes[137] attributes the phenomenon to the conditions affecting the rate of diffusion. He points out that, according to Fick's law of diffusion, the rate of diffusion is greatest where the difference in concentration of the ions in question in two contiguous layers is greatest, that is, just below the front of a precipitation band. As a result, the region near the band decreases in concentration of negative ion, for example, faster than does the space below. Finally, the positive ions have to advance some distance beyond the band to find such a concentration of negative ions that the solubility product of the salt is exceeded and precipitation occurs with the formation of a new band.

The number and variety of the hypotheses that have been offered to account for the formation of Liesgang rings indicate that the process is not a simple one. Since none of the theories that have been proposed seem to take all of the factors into consideration, there is as yet no entirely satisfactory explanation of the phenomenon. Not the least of the objections that have been offered to the hypotheses of Ostwald, Bechold, and Bradford is that the specific effect of the jelly is left out of account. That the nature of the jelly does play an important rôle in certain cases is evidenced by the fact that rhythmic bands of certain salts will be formed only in certain jellies. Thus, silver chromate forms bands in gelatin jellies but not in agar; lead chromate forms bands in agar but not in gelatin; while neither silver nor lead chromate forms bands in silicic acid jelly, although copper chromate does. It seems, however, that investigators have placed rather too much emphasis on the specific effect of the jelly, since rhythmic bands may be prepared without any jelly at all. Thus, Holmes[138] prepared silver dichromate bands in loosely packed flowers of sulfur and Chapin[139] secured distinct bands of ammo-

[136] *Biochem. J.*, **10** (1905), 169.
[137] *J. Am. Chem. Soc.*, **40** (1918), 1187.
[138] *J. Am. Chem. Soc.*, **40** (1918), 1194.
[139] *Cf.* "Exercises in Second Year College Chemistry," 1922, p. 8.

nium chloride by allowing hydrogen chloride and ammonia to diffuse through the air from opposite ends of a tube over 1 m. in length. Holmes' diffusion hypothesis seems to be an important step toward the solution of the problem of rhythmic banding. It should be pointed out, however, that a great deal of work remains to be done before such an important factor for banding as the permeability of the jelly can be accurately formulated.

CHAPTER XVI

THE STUDY OF SOAP SOLUTIONS AND ITS BEARING UPON COLLOID CHEMISTRY

By

James W. McBain

The phenomena met with in the study of soaps are so manifold that it is only by exercise of the severest restriction that a clear, general picture can be obtained. On the other hand, they lend themselves particularly to the study of the colloidal condition and its relation to other states. Soaps are of known chemical composition, and constitute in themselves so numerous a family that almost any desired combination of properties can be obtained. Furthermore, they are typical of a very great group of ionizable materials and they exhibit a particularly close parallelism with the behavior of the salts of protein and gelatin. It has been possible to obtain from these soap solutions unusually definite results, which are of general significance for the understanding of colloids and colloid chemistry. The quantitative results also serve to link together the behavior of colloids with that of ordinary crystalloids.

Soap occurs in five chief forms, the first three of which are properly regarded as solutions, whereas the last two are closely related to a crystallized condition. Whenever the whole of the soap is in either true or colloidal solution, it is clear and transparent or only slightly opalescent. Three such transparent states occur: fluid sol, clear elastic jelly, and clear plastic anisotropic liquid (crystalline liquid). All three are important, the first two on account of their bearing upon the theory of colloids and the structure of jellies, and the third, which still needs much investigation, because of its essential rôle in the processes of soap boiling. The detergent action of soaps is practically confined to the first form. The fourth and fifth forms in which soaps

may occur are as curds and as true crystals (compare photomicrographs, figures 3–7). In the case of the potassium or soft soaps, the crystalline condition is the most stable, whereas sodium soaps are usually opaque masses consisting of white curd fibers, which very often enmesh a saturated soap solution of one of the first three forms. A bar of good toilet soap consists almost exclusively of these extremely fine curd fibers. The parallel arrangement of curd fibers accounts for the "feather" of good household soap. Although many sodium soaps may be temporarily obtained in a crystalline form, these crystals are unfortunately less stable than the curd fibers and are soon replaced by them.

It will clear the ground to state that dilute soap solutions are ordinary crystalloids, whereas more concentrated ones are colloidal electrolytes; and that excess of soap above saturation value separates out in the form of true crystals in the case of potassium soaps and of white curd fibers in the case of sodium soaps. The transparent jellies are confined to a portion of the region in which the soap exists as colloidal electrolyte. The most concentrated solutions, or those to which much salt has been added, are those which constitute anisotropic liquids; and they are immiscible with the other forms of soap.

Soap Sols and the Theory of Colloidal Electrolytes

In the first place, it has been shown that hydrolysis is of negligible significance except in very dilute solution. Indeed, the hydrogen soap, cetyl sulfonic acid, in which hydrolysis is impossible, behaves in most respects exactly like potassium stearate. Hydroxyl ion is a minor constituent of ordinary soap solutions, being present only to the extent of about 0.001N. This has been shown by measurements of:

1. Electromotive force, hydrogen electrode.
2. Catalysis, nitrosotriacetonamine.
3. Conductivity of solutions in contact with insoluble acid soaps.
4. Analysis of the ultrafiltrate of concentrated soap solutions, where nearly all the soap is held back as colloid.

5. Indicators.
6. Electrolytic migration.

We conclude, therefore, with some confidence that the major properties of soap solutions are due to the soap itself and not to products of hydrolysis. There are, then, two properties of soap solutions of great significance; namely, osmotic activity and conductivity.

The osmotic activity was unexpectedly difficult to measure and the well-known work of Krafft and Smits was found to be invalid. However, a wide range of concentrations of many soap solutions has been studied by the following four methods:

1. Lowering of freezing point.
2. Lowering of dew point.
3. Minimum pressure for ultrafiltration through a dense membrane.
4. Lowering of vapor pressure.

The result is that a strong solution of a higher soap may be said to exhibit one-half the osmotic activity of an ordinary salt. Of course, this is much increased in dilute solution and tends to diminish with rise of temperature, and the various soap solutions exhibit every intermediate value in the most regular fashion.

The conductivity is equal to that of a salt. This is attested by hundreds of measurements in which the most careful search has been made for sources of chemical or physical error, and results obtained in other laboratories have confirmed the writer's researches.

There seems to be no alternative to the conclusion that half the conductivity of a soap solution is due to a negative carrier which does not exhibit appreciable osmotic activity and is, therefore, colloidal; that is, the ionic micelle. A colloidal electrolyte is a salt in which one of the ions is replaced by ionic micelles, that is, highly charged and solvated colloidal particles. The undissociated colloidal electrolyte consists of neutral micelles; the ionic micelles essentially of aggregated and hydrated fatty ions.

This interpretation leads to definite values for the concentration of each of the constituents of the solution, such as sodium ion and ionic micelle; and the mobility and equivalent conductivity of the latter follow directly. These values have been confirmed by the following independent methods:

1. Measurement of sodium and potassium ions by sodium and potassium electrodes.

2. Ultrafiltration through membranes which hold back all the colloid and permit all the crystalloid to pass.

3. Measurements of electrolytic migration.

This view of the constitution of soap solutions is also in harmony with a mass of qualitative information. A typical diagram showing the relative proportions of the constituents is that here given for sodium palmitate (Fig. 1).

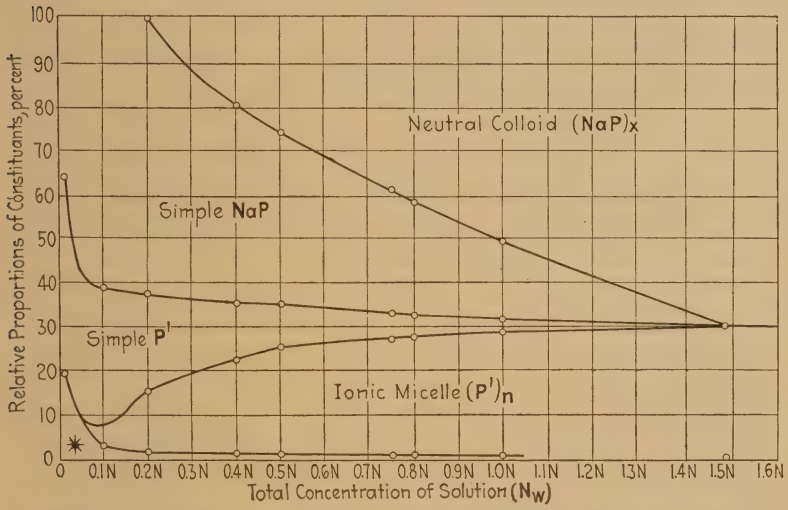


FIG. 1.—The relative proportions of the various constituents of solutions of pure sodium palmitate at 90°. (The asterisk marks the field showing the proportion of acid soap. 2NaP.HP, present.)

Nearly all the ordinary soaps have been studied under a variety of conditions, and it is found that there is but little difference in the amount of neutral micelle in corresponding sodium and potassium salts. On the other hand, in potassium soap solutions, which are always rather more dissociated than the corresponding sodium soaps, the proportion of ionic micelles is always about five-fourths greater than in the sodium soap, and, moreover, the ionic micelles in potassium soaps persists to a dilution about twice as great as in the solutions of sodium soaps. Although the ionic micelle must contain a certain amount of neutral colloid,

there is evidence from ultrafiltration and from migration data that most of the latter exists independently as neutral micelles.

The chief difference between potassium and sodium soaps, and also between the saturated and unsaturated homologous series, is not primarily due to differences in the constitution of their solutions, but rather to the great difference in solubility, the highest saturated sodium soaps being practically insoluble at room temperature, although all are extremely soluble at the boiling point. Dilute solutions are crystalloidal, apart from the colloidal acid soaps arising from hydrolysis, which is prominent in extreme dilution. Formation of colloidal electrolyte is favored by lowering of temperature, increase in molecular weight in the homologous series, and addition of salts.

Theoretical Consequences

1. It is thus established that true, complete, reversible equilibrium can subsist in a colloidal system between all the various crystalloidal and colloidal constituents.

2. There is here a clear proof that the colloidal particles are definite stable aggregates in true equilibrium with their crystalloidal components. The unit is the colloidal aggregate, not the molecule or simple ion, and the aggregate is large enough to be held back by an ultrafilter which allows the molecule to pass through. This throws decidedly unfavorable light upon the recent tendency to assume that the colloidal particles in the closely parallel protein and gelatin systems are merely large molecules which are otherwise in true solution and not aggregated. In the case of soap, each particle of ionic micelle is probably built up around 10 ions which have retained their respective electrical charges.

3. Colloidal particles may conduct much better than true ions. This was our initial suggestion for harmonizing the data for protein systems. But it is necessary to be clear that it is not mere electrophoresis which is meant. The actual conductivity of one ionic micelle containing, say, 10 palmitate ions is 20 or 30 times greater than that of a single palmitate ion; so that the equivalent conductivity of the ionic micelle is still several times that of the simple fatty ion. This is in harmony with the principle underlying Stokes' law.

On the other hand, the osmotic activity of a given number of fatty ions largely disappears when they unite to form a single particle of ionic micelle. It is the usual view of colloid chemists, based on such observations as those of Svedberg and Perrin, that a colloidal particle behaves in this respect like a single molecule, so that if 10 ions go to form 1 ionic micelle its osmotic activity would be diminished tenfold.

4. Consideration of the relationship between a particle of ionic micelle, with its high conductivity, and the corresponding sodium or potassium ions, leads to a modified picture of the electrical double layer and the phenomena connected therewith. It is obvious that the electrical conductivity of these ions and charged surfaces is not impaired by their participation in an electrical double layer. This will be further discussed under a later heading.

5. The discovery of the ionic micelle, the extreme type of a fully charged colloidal particle, brings out clearly the transition through the slightly charged suspensoids to the other extreme of neutral colloids, such as rubber in benzene or nitrocellulose in non-ionizing solvents. It seems clear that the existence and stability of such neutral colloids may be almost or quite independent of electrical charges, and that either solvation or sorption of solvent is the key to their behavior.

There would seem to be some connection between the influence of solvation in stabilizing a particle and the very general rule that mutually soluble substances are chemically similar. The effect of the solvent in disintegrating the solid is the same in both cases.

6. It has been shown that soap in colloidal solution is hydrated, and the method used is of general applicability in colloid chemistry. It consists in the ultrafiltration of a sol to which an indifferent reference substance has been added. The filtrate is more concentrated as regards reference substance than the original sol, and from this the amount of solvent held back in combination with the colloid is readily calculated. Similar values have been obtained from electrolytic migration.

7. In Fig. 2 is shown what appears to be a rational classification of all solutions, showing the gradual transition between each pair of neighboring types.

The connection between suspensoids and colloidal electrolytes calls for further elucidation. The transition which is insisted upon here is the transition in behavior conditioned by the respective proportion of electrical charges. In discussing suspensoids we freely refer to their electrical charges, but almost invariably ignore the equal number of ions of opposite sign which must inevitably

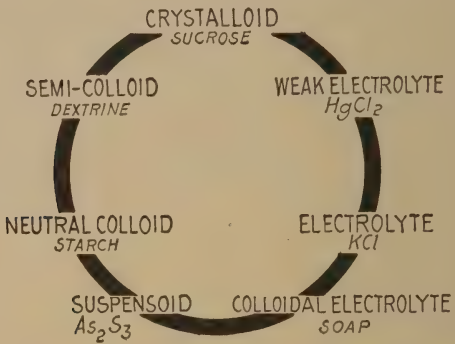


FIG. 2.—A rational classification of solutions, showing the gradual transition between each pair of neighboring types.

accompany them. From the standpoint of the solvent, the properties of a particle do not greatly depend upon whether the particle consists of a chemical compound, whether a single molecule or polymer or aggregate of molecules, or whether the particle consists of a solid kernel only the surface of which has been brought into relationship with the constituents of the solution and the electrical charges of which are, for instance, the result of adsorption on its surface.

It will be shown under a later heading that the transition between suspensoid through colloidal electrolyte to electrolyte is, from the standpoint of the behavior in an electrical field, not merely formal but inherent.

Again, from the standpoint of osmotic behavior, it seems that we have still to realize the full implications of the dictum that a colloidal particle behaves as a single molecule. It would provide a plausible reconciliation between the attempts to apply mass law and phase rule respectively to particles of colloidal dimensions. Both describe the equilibrium between particles and the corre-

sponding single molecules in the solution. For instance, the mass law might be applied to crystalline particles in the form:

$$A_n \rightleftharpoons nA$$
$$(A_n) = K.(A)^n$$

or, in general

$$(A_n)^{\frac{N}{n}} = K_n.(A)^N$$

Concentrations are measured in numbers of particles per unit volume and the chief factor to take into account is the change in number of particles per unit volume and not the actual size of the particles. It is only with the most minute particles of practically molecular dimensions that the value of K_n should reflect any specific tendency to form definite polymers and this factor should be appreciably constant as soon as n has attained, say, two significant figures. Assuming K_n independent of the size of the particles if a large particle of one gram mol (containing N molecules) is cut into N/n particles the number of particles will be increased N/n fold and the concentration of single molecules would have to be increased by $n\sqrt{N/n}$ fold to balance the equilibrium. Taking numerical examples the effect would be about 1/1000th of a per cent for particles 0.1μ diameter and about one per cent for particles of $10\mu\mu$ and of the order of magnitude of 100,000 fold for $1\mu\mu$ diameters. From this hypothesis it would follow that the concentration of single molecules A would be constant to an exceedingly high degree of accuracy as soon as the aggregates, whether solid or liquid, became of visible dimensions, since the number of molecules in 1 g. molecule is 60×10^{22}. On the other hand, solubility and vapor pressure would increase, at first extremely slowly, then rapidly within the region of colloidal dimensions, until, in the special case of molecules so large as to be colloidal, their effective concentration would become identical with the number of particles. The principle here very tentatively made explicit should serve as a useful approximate guide in this field, even if the deviations from the mass law amounted to many fold, since the range of aggregation here contemplated is so enormous (10^{24} fold). It predicts a variation, such as that observed by Hulett and others, in the solubility and vapor pressure with grain size,

although apparently with far finer particles. The phase rule would thus appear in the guise of a special form of the mass law for coarse dimensions, and it provides a mechanism for Bancroft's recent statement that particles, if fine enough, behave as if they were in true solution. Further, it would explain the fact that particles of colloidal dimensions persist indefinitely since their solubility, while still within colloidal range, becomes practically identical with that of massive material.

Independence of Classical Dissociation Theory

It is essentially for the sake of convenience that the results have been discussed in terms of the Arrhenius dissociation theory. The same conclusions follow if the conceptions of the 100 per cent ionization hypotheses are employed. Practically only the interpretation of the crystalloidal soap is affected, since now the crystalloidal part of soap might be considered 100 per cent ionized. To a very large extent, although not entirely, the Arrhenius and the 100 per cent theories are interchangeable methods of describing the undisputed facts of ordinary electrolytes. Whichever theory is employed, the striking fact is at once encountered that, in spite of the high conductivity, soap exhibits far smaller osmotic effects than that expected of the whole group of uni-univalent electrolytes, such as potassium chloride. This corresponds with cations of ordinary, and anions of negligible, activity. Low activity is characteristic of high valency—the ionic micelle. Direct experimental confirmation is obtained from experiments on ultrafiltration. It should be remembered, too, that the 100 per cent ionization hypotheses are admittedly inapplicable to weak or complex electrolytes, such as, for example, cadmium iodide where, during electrolysis, cadmium migrates towards the anode. Even crystalloidal soap in dilute solution is by no means as strong an electrolyte as any of the ordinary uni-univalent salts.

Colloidal Electrolytes

There is evidence that colloidal electrolytes constitute an enormous class of substances, probably as numerous as acids and bases put together, occurring both in aqueous and non-

aqueous solutions. Indeed, they would appear to be particularly important in non-aqueous solutions, although this probability has so far been entirely neglected in the published literature. Silver bromate and diethylamine constitute a good example, which the writer has investigated. The characteristics of this class are essentially the occurrence of polymolecular aggregates and ionic micelles.

Some of the very numerous substances which must be recognized as belonging to this group are the proteins and gelatin salts, dyes, indicators, the higher sulfonic acids and hydrochlorides, silicates, telurates, and many inorganic substances—in fact, most substances of high molecular weight or containing long carbon chains which are capable of splitting off an ordinary ion.

Congo red was simultaneously investigated by Donnan and Bayliss. The work of Donnan and Harris,[1] in agreement with that of Bayliss[2] and Biltz and Vegesack,[3] shows that the osmotic pressure of Congo red is considerable, but does not exceed that of a simple non-electrolyte. On the other hand, the conductivity was unexpectedly high, being nearly equal to that of sodium chloride. Donnan's interest was chiefly attracted to the important theory of membrane equilibria, which he thought might be sufficient explanation of the discrepancy, since the sodium ions were not expected to contribute in the ordinary way to the osmotic pressure. He discussed the formation of high complexes such as $(Na_2R)_{20} \rightleftarrows 20Na + (NaR)^{20'}_{20}$, but added, "it is difficult to reconcile such an assumption with the high values obtained for the molar conductivities."

On the other hand, Bayliss writes, after making various alternative suggestions:

> The possibility of aggregated simple ions carrying the sum of the charges of their components is suggested in order to explain the experimental results. . . . These large organic ions may aggregate while retaining the combined charges of their components. This seems to imply, however, so great a density of the charge on the surface of the aggregates as to be improbable. . . . The difficulty as to

[1] *Trans. Chem. Soc.*, **99** (1911), 1554.

[2] *Proc. Roy. Soc.*, B, **84** (1911), 229 and earlier papers.

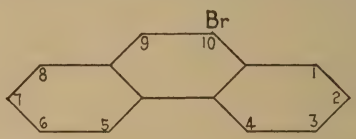
[3] *Z. physik. Chem.*, **73** (1910), 481; **77** (1911), 91, etc.

the large charge on the aggregated anion remains. . . . It may be tentatively suggested that aggregation of molecules may play some part in the mode of ionization.

The existing data for other dyes and for indicators are of a similar nature and may be similarly accounted for. Many of the unexplained reactions of indicators, particularly with reference to the sometimes enormous effect of neutral salts, are now seen to be probably due to disturbance of the equilibria between colloid and crystalloid and, hence, between the various possible crystalloidal forms of the indicator radical. We have proved that such true equilibria occur, and that every change in the colloid determines a corresponding alteration in the position of equilibrium.

Miss Norris[4] has in this laboratory compared the properties of cetyl sulfonic acid ($C_{16}H_{33}SO_3H$) with those of the soaps. The properties and the equilibrium diagram are found to bear a detailed resemblance to the behavior of the higher soaps, such as potassium stearate.

Another group of sulfonic acids prepared by Sandqvist[5] are the derivatives of 10 bromo- and 10 chloro-phenanthrene:



With the Br at 10 and sulfonic acid group at 6, the behavior is apparently identical with that of soaps. In dilute solution the acid behaves like an ordinary electrolyte. With increase in concentration the solution becomes more and more colloidal in character and ultimately the isotropic solution becomes anisotropic. Decreased temperature has the same effect as increase of concentration. Addition of strong acids produces much the same effect as increase of concentration. Viscosity increases very rapidly with concentration but the electrical conductivity remains approximately normal, even when the viscosity has become very large. Lowering of freezing point is deficient in more

[4] *Trans. Chem. Soc.*, **121** (1922), 2161.

[5] *Ber.*, **48** (1915), 2054; *Kolloid Z.*, **19**, (1916), 113; *J. Chem. Soc.*, **110** (1916), 556; *Ann.*, **417** (1918), 1; 17.

concentrated solution. The corresponding chloro-derivative is apparently much more colloidal, as judged by its much greater viscosity, and is also much more anisotropic. The 10 bromo 3 sulfonate forms yellow flocculent solutions.

This brings us to the great influence of the shape of the molecule on the capacity for forming colloidal electrolytes and anisotropic liquids. The soaps are all long-chain compounds. Of two similar organic compounds, it is the long molecule which is colloidal, while the more rounded or symmetrical form is much less so or not at all. For instance, in Sandqvist's compounds, if the bromine is replaced by a second sulfonic acid, the solutions are neither colloidal nor anisotropic. Or again, if two molecules of the bromo sulfonic acid become linked together in the 10 position through oxidation and elimination of bromine, the viscosity is almost completely lost. Similar observations have been made when comparing the sodium salts of α and β naphthalene sulfonates.[6]

The Existence and Properties of Soap Jellies

The salient facts observed by Miss Laing are the following: The conductivity of a soap solution is quantitatively unaffected when it sets to a clear, transparent, elastic gel. The same is true of its osmotic activity, as measured by lowering of vapor pressure, and of the concentration of sodium ions measured by the sodium electrode. Indeed, the only difference between sol and gel appears to be the mechanical rigidity and elasticity of the latter. Neither shows any structure in the ultramicroscope. During electrolysis the relative movement of the constituents of the solution is independent of whether it is a clear, elastic jelly or a fluid sol.

The Structure of Jellies

1. The identity of the significant properties of sol and gel proves that the same equilibria exist in each. The colloidal particles in sol and gel must be identical in kind and amount.

[6] *Trans. Chem. Soc.*, **121** (1922), 2167.

2. The unchanged conductivity shows that the process of electrical conduction is unchanged in kind and degree.

3. The identity of conductivity of sol and gel is particularly significant in discussing the structure of gels. Any theory conflicting with this is evidently untenable, as, for instance, Wo. Ostwald's and M. H. Fischer's suggestion that gelatinization is due to reversal of phases; similarly, with a closed honeycombed structure, or even an only partly open structure. Some micellar theory of gels is clearly indicated. In the case of soaps the structure is probably filamentous.

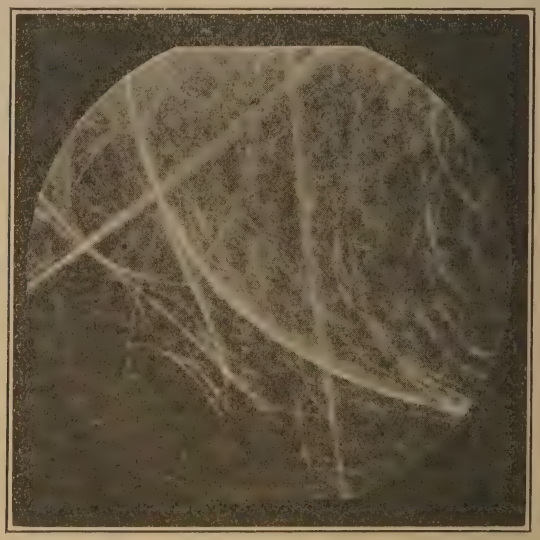


FIG. 3.—1.0 N Sodium laurate. Curd fibers appearing during cooling. (Magnification 600 diameters.)

4. Thus, although soaps, proteins, etc. are commonly called emulsoid colloids, they cannot be regarded as emulsions.

5. Once more, there is strong evidence that the colloidal unit is an aggregate of molecules, and that these colloidal units persist and retain their identity in larger structures, such as gels and coagula. This behavior appears to be general; compare, for instance, the study of particulate clouds (aerosols).

6. The apparent viscosity of such systems as soap and gelatin solutions has no marked effect upon electrical conductivity; the

viscosity of a soap sol may be altered a thousand fold, or it may be solidified to a clear, elastic jelly without affecting the molar conductivity.

The Properties of Soap Curds

These white opaque systems form a complete contrast to soap jellies. Under the ultramicroscope it can be seen that the formation of a soap curd is due to the separation from solution of microscopic or ultramicroscopic fibers, which may be of very great length and which have been shown to consist of neutral hydrated sodium soaps. Hydrated sodium soaps in their solid stable form consist of these curd fibers, whereas hydrated potassium

Fig. 4.—0.05 N Sodium behenate. Showing freshly formed curd fibers. (Magnification 600 diameters.)

soaps form true lamellar crystals, the fibrous form being evanescent and unstable. A few curd and crystalline forms are shown in Figs. 3 to 7. The curd fibers possess a very high temperature coefficient of solubility, so that a commercial soap usually consists of such fibers enmeshing a soap sol or gel of the more soluble soaps. Formation of curd from a solution progres-

sively lowers the conductivity to a value corresponding to the solubility at that particular temperature. The osmotic activity is similarly diminished, and the results are confirmed by the analysis of the expressed liquid.

According to recent X-ray work of Piper and Grindley[7] the curd fibers of sodium palmitate are built up from molecules of soap laid parallel to each other and placed end to end so that sodium comes next to sodium and paraffin chain is end on to paraffin chain. There are thus sheets of double sodium atoms 44Å (4.4$\mu\mu$) apart; that is, just twice the length of the single molecule as determined by Langmuir in his monomolecular films. Curd fibers are probably to be regarded as true crystals. It is important to note that anisotropic soap solutions give no such X-ray pictures; these are confined to crystals and curds.

The chief theoretical result is the sharp distinction between true soap jellies, anisotropic liquids, and the soap curds with which they have been commonly confused. Gelatinization is not a process of crystallization in the sense of removal of colloidal particles from the sphere of action of the solvent, whereas the formation of curd or coagulum involves this separation. Presumably, jellies in general should be distinguished from coagula.

The Conduction of Electricity in Colloidal Systems

Movement of charged carriers is identical with electrolytic conductivity. All carriers, whether ions, particles, or surfaces, must, therefore, impart conductance to the system. The ionic micelle was postulated and discovered on the ground of its high conductivity. This is only a particularly striking case of an "electrical double layer" where the conductivity of both parts of the double layer has been at last taken into account and it clearly indicates that the electrical conductivity of ions and surfaces is unimpaired in an electrical double layer. This at once brings the whole problem of electrophoresis into the field of electrolytic migration.

What is involved in every case is the relative movement between solvent and carrier, whether this relative movement be

[7] *Proc. Physical Soc.*, **35** (1923), 268.

envisaged as electrophoresis, electro-osmosis, or ionic migration. Miss Laing has carefully investigated sodium oleate sols, gels, and curds. She finds that the "electrolytic migration" in soap solutions consists of strictly identical processes with "electro-osmosis" of water through a transparent soap jelly and with the

FIG. 5.—1.0 N Potassium elaidate. Between crossed nicols showing fibers and true crystals. (Magnification 120 diameters.)

"electrophoresis" of pieces of soap jelly suspended in a soap solution. In each case the relative movement of, for instance, sodium and water is the same.

A general formula

$$n_1 = \frac{c_1 m_1 f_1}{\mu}$$

expresses the actual movement relative to the solvent of each constituent of any electrically conducting system, whether homogeneous or heterogeneous, electrolytic, colloidal, or involving electrical double layers or diaphragms. The movement of the solvent relative to any conducting constituent is $\frac{m_1 f_1}{\mu}$ kilos of solvent per faraday of current and is termed "electro-osmosis." n_1 is the number of chemical equivalents transported per faraday

of current; c_1 is the concentration of that constituent in chemical equivalents per kilo of solvent; m_1 is the number of chemical equivalents which carry one electrical charge, whether positive or negative; f_1 is the electrical conductivity per electrical charge, so that $m_1 f_1$ is the effective mobility; and μ is the total conductivity of the solution and is equal to the sum of the concentrations of each conducting constituent multiplied by its mobility. From this standpoint, the only distinction between colloid and crystalloid is the number of chemical equivalents which are associated with one electrical charge. The effective mobility $m_1 f_1$ appears to be of the order of magnitude of an ordinary ion, although f_1 is usually very minute.

FIG. 6.—2.25 N Potassium laurate. Between crossed nicols, showing "liquid crystals" in isotropic medium. (Magnification 100 diameters.)

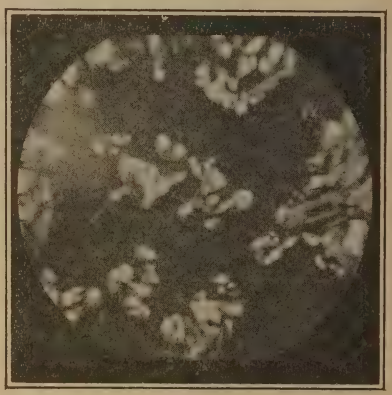


FIG. 7.—3.0 N Potassium laurate. Between crossed nicols, showing "liquid crystals" on cooling after melting. (Magnification 100 diameters.)

It was pointed out by Müller[8] in 1907 that the electrophoretic mobility of a colloid expressed in centimeters per volt per centimeter per second is almost as great as that of a slow-moving organic ion, which is exactly what is found here for undissociated colloidal soap, in spite of its negligible conductivity.

Using the new formula and recognizing that undissociated soap moves one-third as fast as the ionic micelle, it was possible quantitatively to predict all the values for curds even when the

[8] "Allgemeine Chemie der Kolloïde."

transport exceeded five equivalents of oleate per faraday of current.

Obviously, migration experiments, whether by the Hittorf or direct method, do not measure the conductivity or true mobility of a colloidal particle but only its effective mobility or electrophoresis $m_1 f_1$. Direct support for these views has been obtained from a study of the conductivity of potassium chloride in capillary cells made of quartz.

This has led to a new conception of the electrical double layer. The mobile ions involved in all electrokinetic phenomena are very sparsely distributed and cover less than one tenth of a per cent of the surface. The contact potentials hitherto deduced are shown to possess but a fictitious and ambiguous significance, and the assumption made in all previous mathematical treatment of this subject appear to require radical revision.

In conclusion, it is seen that an adequate elucidation of the manifold and definite properties of soap solutions will have a direct bearing upon a surprisingly large number of theoretical considerations.

REFERENCES

1. McBain, James W. and Taylor, Millicent: Zur Kenntnis der Konstitution von Seifenlösungen Lösungen von "Natriumpalmitaten," *Z. physik. Chem.*, **76** (1911), 179.
2. McBain, James W. and Taylor, Millicent: Über die elektrische Leitfähigkeit von Seifenlösungen, *Ber.*, **43** (1909), 321.
3. Cornish, E. C. V.: Dichtigkeitsmessungen der Seifenlösungen, *Z. physik. Chem.*, **76** (1911).
4. Bowden, R. C.: Studies of the constitution of soap in solution: the electrical conductivity of sodium stearate solutions, *Trans. Chem. Soc.*, **99** (1911), 191.
5. McBain, James W., Cornish, E. C. V. and Bowden, R. C.: Studies of the constitution of soap in solution: sodium myristate and sodium laurate, *Trans. Chem. Soc.*, **101** (1912), 2042.
6. McBain, J. W.: "The Mobility of Highly Charged Micelles," *Trans. Faraday Soc.*, **9**, (1913), 99; *Kolloid-Zeitschr.*, **12**, (1913), 256.
7. Bunbury, H. M. and Martin, H. E.: Studies of the constitution of soap solutions: the electrical conductivity of potassium salts of fatty acids, *Trans. Chem. Soc.*, **105** (1914), 417.
8. McBain, J. W. and Martin, H. E.: Studies in the constitution of soap solutions: the alkalinity and degree of hydrolysis of soap solutions, *Trans. Chem. Soc.*, **105** (1914), 957.

9. Laing, M. E.: The state of potassium oleate, and of oleic acid in solution in dry alcohol, *Trans. Chem. Soc.*, **113** (1918), 435.
10. McBain, James W. and Bolam, T. R.: The hydrolysis of soap solutions, measured by the rate of catalysis of nitrosotriacetonamine, *Trans. Chem. Soc.*, **113** (1918), 825.
11. Beedle, F. C. and Bolam, T. R.: The hydrolytic alkalinity of pure commercial soaps, *J. Soc. Chem. Ind.*, **40** (1921), 27T.
12. McBain, James W.: Colloidal electrolytes: soap solutions as a type, *J. Soc. Chem. Ind.*, **37** (1918), 249T.
13. McBain, James W., Laing, M. E. and Titley, A. F.: Colloidal electrolytes: soap solution as a type, *Trans. Chem. Soc.*, **115** (1919), 1279.
14. McBain, James W. and Salmon, C. S.: Colloidal electrolytes. Soap solutions and their constitution, *J. Amer. Chem. Soc.*, **42** (1920), 426.
15. McBain, James W. and Salmon, C. S.: Colloidal electrolytes. Soap solutions and their constitution, *Proc. Roy. Soc.*, **A, 97** (1920), 44.
16. McBain, James W.: Colloids and colloidal electrolytes, *Nature* (March 10, 1921), 46.
17. McBain, James W.: A novel magneto effect, *Nature* (March 17, 1921), 74.
18. Laing, M. E. and McBain, James W.: The investigation of sodium oleate solutions in the three physical states of curd, gel, and sol, *Trans. Chem. Soc.*, **117** (1920), 1506.
19. McBain, James W. and Taylor, Millicent: The degree of hydration of the particles which form the structural basis of soap curd, determined in experiments on sorption and salting out, *Trans. Chem. Soc.*, **115** (1919), 1300.
20. McBain, James W. and Martin, H. E.: The hydration of the fibers of soap curd. Part I. The degree of hydration determined in experiments on sorption and salting out, *Trans. Chem. Soc.*, **119** (1921), 1369.
21. McBain, James W. and Salmon, C. S.: The hydration of the fibers of soap curd. Part II. The dew-point method, *Trans. Chem. Soc.*, **119** (1921), 1374.
22. Laing, M. E.: The hydration of the fibers of soap curd. Part III. Sorption of sodium palmitate, *Trans. Chem. Soc.*, **119** (1921), 1669.
23. King, A. M.: The effect of high concentration of salt upon the viscosity of a soap solution, *J. Soc. Chem. Ind.*, **41** (1922), 147T.
24. McBain, James W., Taylor, M. and Laing, M. E.: Studies of the constitution of soap solutions, solutions of sodium palmitate, and the effect of excess of palmitic acid or sodium hydroxide, *Trans. Chem. Soc.*, **121** (1922), 621.
25. Salmon, C. S.: Direct experimental determination of the concentration of potassium and sodium ions in soap solutions and gels, *Trans. Chem. Soc.*, **117** (1920), 530.
26. Salmon, C. S.: Note on the effect of electrolytes on the constitution of soap solutions, as deduced from electromotive force, *Trans. Chem. Soc.*, **121** (1922), 711.

27. Darke, W. F., McBain, J. W. and Salmon, C. S.: The ultramicroscopic structure of soaps, *Proc. Roy. Soc.*, **A, 98** (1921), 395.
28. McBain, J. W.: Colloid chemistry of soap. Part I. Solutions. *Third Report on Colloid Chemistry, British Association for the Advancement of Science* (1920), pp. 1–31. Reprinted in serial form in the *Oil and Trade Colour Journal* (1921), and the *Seifensieder Zeitung* (1921).
29. McBain, J. W. and Walls, E.: The colloid chemistry of soap. Part II. The soap boiling processes, *Fourth Report on Colloid Chemistry, British Association for the Advancement of Science* (1922), pp. 244–263.
30. Flecker, O. J. and Taylor, M.: Studies of the constitution of soap solutions. Sodium behenate and sodium nonoate, *Trans. Chem. Soc.*, **121** (1922), 1101.
31. McBain, J. W. and Burnett, A. J.: The effect of an electrolyte on solutions of pure soap. Phase rule equilibria in the systems: sodium laurate-sodium chloride-water, *Trans. Chem. Soc.*, **121** (1922), 1320.
32. Norris, M. H. and McBain, J. W.: A study of the rate of saponification of oils and fats by aqueous alkali, under various conditions, *Trans. Chem. Soc.*, **121** (1922), 1362.
33. McBain, J. W. and Jenkins, W. J.: The ultrafiltration of soap solutions. Sodium oleate and potassium laurate, *Trans. Chem. Soc.*, **121** (1922), 2325.
34. McBain, J. W., Harborne, R. S. and King, A. Millicent: A method of determining the detergent action of soaps, *Chem. Ind.* **42** (1923) 3731.
35. McBain and Darke: *Trans. Faraday Soc.*, **16** (1920–21), 150.
36. McBain, J. W.: A general conception of neutral colloids, and its bearing upon the structure of jellies. *Trans. Faraday Soc.*, Nov. 5, 1923.
37. Laing, M. E.: A general formulation of movement in an electric field. Migration, electro-phoresis, and electro-osmosis of sodium oleate. *J. Phys. Chem.*, **28** (1924).
38. McBain, J. W.: The conception and properties of the electrical double layer, and its relation to ionic migration. *J. Phys. Chem.*, **28** (1924).

CHAPTER XVII

VISCOUS AND PLASTIC FLOW IN COLLOID SYSTEMS

By

Eugene C. Bingham

When Graham called the viscometer a colloidoscope, he was epigrammatically calling attention to the unique importance of flow in determining the properties of colloids. In our older science, properties like melting point, boiling point, solubility, and elasticity have played a rôle the importance of which can scarcely be overrated. Our science has very largely developed out of the possibility of isolating substances in which these properties are sharply defined. The absence of these control properties in the newer colloid chemistry has constituted a distinct handicap. The search for such control properties holds out, as a result of its successful conclusion, the promise of rapid development in the newer science.

Apparent Viscosity

Whereas the character of the flow of colloids was very early recognized as important, it must be admitted that as a control property viscosity has also failed to meet our proper expectations. Various investigators have called attention to the fact that the viscosity of many colloids is not constant but highly dependent upon the rate of shear. Elaborate investigations have served to prove that this difficulty does not appear when dealing with homogeneous liquids or gases. It is, therefore, peculiar to colloids, although it may not be characteristic of all colloids. Since viscosities are of little value unless exactly definable, we come at once to the conclusion that, *when one is dealing with the flow of colloids, it is of first importance to determine whether the viscosity is independent of the shearing stress.* When the so-called "viscosity" varies with the shearing stress, it becomes merely an

apparent viscosity, which is not a constant of the material but a variable with very wide limits.

A clue to this anomaly in the flow of colloids was found by a study of the shear obtained with shearing stresses of different magnitude. For the understanding of this, we will now proceed to a consideration of the different types of deformation under shearing stress.

Types of Flow

Let us consider a parallelopiped of material $ABCD$ confined between the imaginary planes AB and CD, as shown in section in Fig. 1, and acted upon by a shearing stress on either of the two planes of F dynes per square centimeter. Furthermore, let us suppose that the distance between the planes is represented by r. Several things may happen.

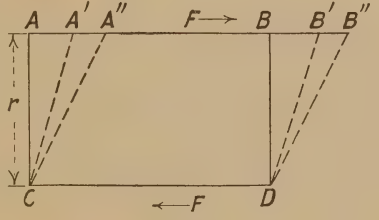


Fig. 1.

The points in the plane AB may *immediately* move over in the direction of the shearing stress by a distance AA', each layer of the material taking its part in this deformation in direct proportion to its distance from the plane CD. It is characteristic of this type of deformation that it quickly reaches its final value and does not increase further unless the shearing stress is increased. On the other hand, if the shearing stress is removed, the material springs back to its initial position. The elastic deformation $AA' = s$ follows the law first enunciated by Hooke

$$s = Fer \qquad (1)$$

where e is the coefficient of elasticity. In the limiting case, where the elasticity is zero, there would be no deformation and the material would be said to be perfectly rigid. It is to be particularly noted that elastic deformation does not depend upon the time factor.

In another case, after the first elastic deformation, it is found that the deformation increases steadily with a constant velocity

v, which is maintained as long as the shearing stress is applied. This viscous deformation follows the law

$$v = F\varphi r \tag{2}$$

where φ is the coefficient of fluidity. This law applies to all fluids, or perhaps it would be more nearly correct to state that substances are to be regarded as fluids which obey this law. Viscous deformation increases with the time. Glass and pitch are to be regarded as viscous liquids, since they obey the above law, whereas paint and butter are to be regarded as soft solids, because they do not obey it. According to this conception, the properties of fluidity and elasticity are quite independent, and fluids as well as solids may show an instantaneous elasticity of shape.

When substances do not undergo continuous deformation at a given shearing stress, they may yet do so at a slightly higher stress. If a certain shearing stress f, called the "yield value," is required to start the flow, and thereafter the deformation is proportional to the excess of shearing stress applied, we have

$$v = (F - f)\mu r \tag{3}$$

where μ is called the mobility of the material. This has been proposed as the fundamental law of plastic flow. As in the case of viscous flow, plastic flow is dependent upon the time.

For the sake of completeness, the theoretical case should here be referred to in which no continuous deformation takes place before the ultimate strength of the material is exceeded. But since, in *rupture*, the material does not flow, it is not necessary to comment upon it further in a discussion of flow.

In the study of flow, a complication arises in that these different types of deformation may take place simultaneously and lead to confusion. For example, it is well known that no substance obeys Hooke's law perfectly, even far below the yield point. There is some deformation taking place which is increasing with the time, even when the shearing stress is very small. It must be ascribed to viscous flow. When this deformation is appreciable, we have the indefinitely defined "elastic limit." Above the yield point plastic flow begins, but it is doubtless associated in some way with the viscous deformation which manifested itself

at the lower stresses. If this mixed flow manifests itself in an *apparently* homogeneous substance like zinc, it is not surprising that it becomes quite evident in a heterogeneous substance like paint. In fact, it is because the solid and liquid phases of a mixture tend to flow through capillary spaces at different rates when subjected to shearing stress, that the use of the filter press is feasible in separating, let us say, oil from the oil cake. For want of a better term, this viscous flow of the dispersion medium through and ahead of the disperse phase has been referred to as *seepage*.

One of the results of this mixed flow is that when the rate of flow is plotted against the shearing stress, curves are obtained which are not linear throughout their entire length, *ABC* in Fig. 2; they rather bend off toward the origin, as *BD*. As would be expected, the seepage is most noticeable in the neighborhood of the yield value. Were the flow of plastic materials below the yield value entirely viscous, the curve *BD* would be linear as demanded by equation (2), so the curve proclaims the fact which is proved also by experiment that the entire material is deformed in this kind of flow.[1] As the shearing stress is increased, the plastic flow becomes more and more important in comparison with the slow seepage. In the cases thus far investigated, the flow-stress curves become more and more nearly linear, as required in true plastic flow, equation (3). The yield value is then found by extrapolating the curve *AB* to the point *C* in the figure.

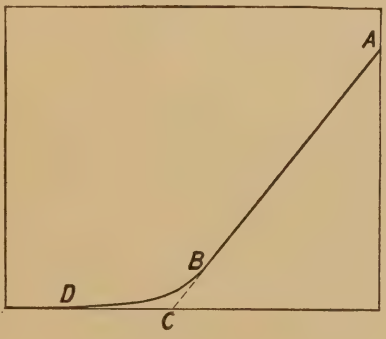


FIG. 2.

Whereas the above view has seemed to be the simplest and most obvious one to take, the writer has no desire to be dogmatic, and refers the inquiring reader to the critical study of the subject by E. Buckingham.[2] Along with the complication due to seep-

[1] *Cf.* discussion of pseudo-plastic flow later.

[2] *Proc. Am. Soc. Testing Materials*, **21** (1921), 1154.

age, we should most certainly refer to *slippage*.[3] Since this has not even yet been measured in any well-authenticated case, it may be passed over with a mere reference[4] for the reader and a caution to the experimenter.

If one constituent of the plastic material resists continuous deformation at the same time that another constitutent is continually giving way, the shearing stress exerted on the first portion must steadily increase and, therefore, the elastic deformation in this constituent will also increase with the time elapsed; and if, after some time, the shearing stress is removed, a most peculiar effect is to be observed. The elastic deformation should immediately disappear, as stated above, but, due to the seepage, it is clearly impossible for all of it to disappear until seepage has taken place again in the opposite direction. The result is that there is an immediate partial recovery followed by a slow recovery known as the *elastic after-effect* of Weber. The strains accumulated in a solid as a result of various attempts to shear the material may greatly affect the deformation produced by a given stress, as is thoroughly well known to metallurgists.

We are then able to distinguish the following independent properties and their reciprocals, which appear to be sufficient to characterize the different types of flow:

e = elasticity, the reciprocal of n = rigidity
φ = fluidity, the reciprocal of η = viscosity
μ = mobility, the reciprocal of ξ = consistency

The term "consistency" has heretofore been used loosely and there is as yet no general agreement to give it the above exact meaning. But the tendency of an advancing civilization is to give to words more precise meanings, and so to say, for example, that a substance has the consistency of butter is offensive so long as consistency cannot be quantitatively defined, and it appears quite certain that the properties of butter which determine its flow depend in an extraordinary degree upon the

[3] Hydraulic flow and flow through orifices should also be referred to, although information on these types, mostly with liquids, leads to the belief that no new property of matter is involved.

[4] BINGHAM, E. C.: "Fluidity and Plasticity," McGraw-Hill Book Co., 1922, pp. 20 *et seq.*

temperature. The use of an exact definition should in no way lessen the real value of the loose use of the word, and the exact use of the term will always be understood whenever a numerical value is used. There is a body of opinion indicating that consistency is a measure of resistance to rapid deformation, and this is the sense in which the term is here employed. There is a considerable advantage in using a term which is already familiar.

The Significance of Plasticity Measurements

Now that the anomaly referred to at the beginning of this chapter has been explained through the clear differentiation between viscous and plastic deformation, it seems proper to consider some of the possible ways in which a knowledge of the yield value and mobility may supply useful information.

The Melting or Softening Temperature in Colloids.—When a colloidal substance, such as asphalt or butter, is heated it becomes soft, and efforts without number have been made to determine the melting points of such materials, and, by following a carefully specified procedure, it is sometimes possible to assign to a given substance a number which can be closely duplicated. But the value obtained depends in a high degree upon the exact procedure followed and, upon practical as well as theoretical grounds, it may be doubted whether these substances have a definite melting point. Presumably with this in mind, other names have been suggested, such as the "softening temperature." Regardless of the name that may be given it, which is of relative unimportance, it is highly desirable that the constant involved should be definitely determinable. To fulfil this requirement it is not sufficient that the numerical constant can be duplicated by following a closely specified procedure with a given apparatus. To have the widest usefulness the value of the "constant" should not be dependent in any way upon the dimensions of the apparatus or of the procedure used.

Take the simple case of two substances A and B, which are partially soluble, the one in the other, and form a eutectic, as represented in Fig. 3. A given mixture having the concentration C will be entirely in solution at an elevated temperature, but on cooling to D it will reach saturation and under favorable circum-

stances the solid phase of B will make its appearance and, simultaneously with the appearance of the new phase, the material will display a yield value under suitable conditions. In other words, the transformation from fluid to solid takes place at the point D, and this temperature is the analogue of the melting point. As the cooling is continued, the amount of the solid phase B increases, but since the crystals may be separated from each other

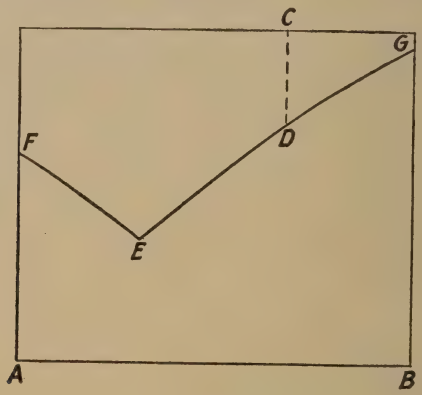


FIG. 3.

by the remaining liquid phase until the point E is reached, we may be prepared to find the material to be a "soft solid," if subjected to test on the plastometer. At the eutectic temperature E the liquid phase disappears and a new type of solid phase appears. If there is plastic deformation possible, it must be based on the deformation of one or both of the solid phases, whereas before, the deformation was largely, if not exclusively, in the liquid phase. The yield value and mobility temperature curves, therefore, both show a discontinuity at the eutectic temperature.

From this point of view, one would expect the plasticity data to give information similar to that obtained from the cooling curves, but not in agreement with other conventional means for determining the so-called melting point, some of which may be described briefly.

The method recommended for butter by Dr. Wiley consists in floating thin discs of butter between layers of water and alcohol and then raising the temperature until the butter draws itself up into spheres.

In the ball-and-ring test of the melting point (A. S. T. M. D36–21) a steel ball is used to force out the material which is supported in a brass ring. Raising the temperature at the exact rate of 5°C. per minute, the melting point is taken as the temperature at which the material is extruded from the ring 2.54 cm.

In the Saybolt melting point apparatus a series of small wooden sticks are held in place by means of the plastic material in well holes drilled in a brass plate which can be immersed in a vessel containing water. The melting point is taken as the temperature at which the sticks are released and rise to the surface of the water, the bath being raised in temperature at a rate of from 0.5 to 1.0°F. per minute.

Still another method by Pohl consists in dipping a thermometer into the molten material, withdrawing it, and allowing the material to solidify on the bulb of the thermometer, after which the temperature is again raised at the rate of 1°F. per minute until the first drop leaves the thermometer.

In these last methods it is evident that plastic flow is taking place. In one case the shearing stress is derived from the interfacial tension, in another from the weight of the ball, in another from the buoyant force acting upon the sticks, and in the last from the weight of the material itself. Since the shearing stress is very different in the different methods, and since, therefore, the flow must take place while the yield value has a finite value, it seems possible that the temperatures obtained may be quite anomalous, depending as they do upon the yield value and the mobility, as well as upon the time of heating. We may even imagine that, given two substances A and B, with one instrument the substance A will appear to be the softer of the two, whereas with another instrument the substance B will appear to be softer than A. The reason for this behavior is made clear in Fig. 4 where the rate of deformation for the substance A is greater than that of B at the shearing stress F', whereas the reverse is true at the shearing stress F''.

As an example of this type of substance, butter may serve as an example. The fluidity temperature curve is linear from 35 to 50°. But at 35.7°C. there is a discontinuity. Below that temperature there is found a yield value which increases in a linear manner as the temperature is lowered. At 35.7° the fluidity

is approximately 2.5 and the fluidity of the undercooled liquid butter at 32° is 2.0, but the mobility falls off very rapidly and reaches a value of only 0.0005 at 32°. At 17.3° the mobility seems to reach a zero value, and we have found that at 10° we were unable to obtain true plastic flow with the pressure available. There was, however, some oil squeezed out by seepage which would not solidify at 10°.

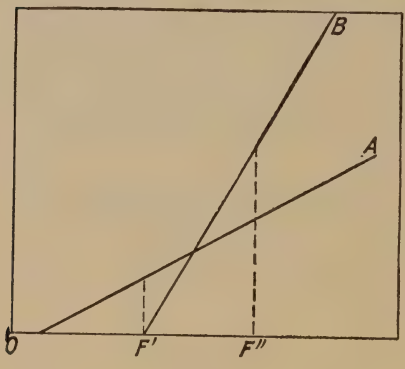


FIG. 4.

There is one fundamental difference between the cooling curve method and the plasticity method. The success of the former depends upon the assumption that equilibrium at each temperature is secured during the time required for the cooling to take place. With the plasticity method no such assumption is necessary, for as many determinations of the plasticity may be made as are desired. With butter, for example, it has been found that, even with seeding and thorough stirring, the time required for reaching equilibrium may run into hours.

On solidification, new molecules must diffuse up to the face of the crystal as rapidly as the liquid bathing the crystal is impoverished, and this rate of diffusion is directly proportional to the fluidity of the medium. The difficulty still remains if the temperature of experiment is reached by raising the temperature instead of by a process of cooling, for, as the solid phase dissolves, it is necessary for the dissolved molecules to diffuse into the solution in order that the process of solution may continue. If the temperature could be raised so rapidly that diffusion did not result, we may even conceive of a mixture remaining plastic up to the temperature of melting of the highest melting component.

The "Solubility" of Colloids.—Having shown that the plasticity method may give sharp control points for colloids which are at least the analogues of the eutectic temperature and melting point, or better, saturation point of true solutions, we will proceed to the consideration of plasticity and the so-called solubility of

colloids. When it is said that nitrocellulose is more soluble in acetone, let us say, than in butyl acetate, the statement does not mean what such a statement does in classical chemistry. In the first place, the solution is not a true solution at all in either solvent, so far as is definitely known and, therefore, these substances do not form a saturated solution, which can be measured. If, with this idea in mind, we abandon the term solubility and say that acetone peptizes a certain nitrocellulose, whereas water alone does not, we may have gained something in precision, but our knowledge is very unsatisfactory, since it cannot be expressed quantitatively. When it is stated that nitrocellulose is more soluble in acetone than in butyl acetate, it appears to be based in some way upon the fact that for a solution of the same concentration the solution in acetone flows the more readily. Since, however, acetone has a considerably higher fluidity than butyl acetate this is what we would expect, and we find ourselves in the possession of nothing more than a possible clue to the problem.

Since all solutions of nitrocellulose appear to be plastic, the the terms "viscosity" and "fluidity" must be avoided. We come then, to a study of the yield value and mobility of these solutions. Hyden, Ross, and the author have studied solutions of Newburgh nitrocellulose in acetone and a 60 per cent diethyl ether and 40 per cent ethyl alcohol mixture by weight. For a 5 per cent solution of nitrocellulose at 20°C. the following values of the yield value and mobility were obtained as compared with the fluidity of the pure solvent:

Solvent	Fluidity	Yield value	Mobility
Ether-alcohol	250.00	11.50	0.86
Acetone	310.00	8.00	1.99
Ratio	1.24	1.43	2.31

If the solubility is merely a matter of the fluidities of the pure solvents, then we should expect to find the mobilities in the two solvents to have the same ratio as the fluidities of the solvents themselves. From the above table it is evident that the mobility in acetone is far greater than we should expect. This and

other facts not yet referred to indicate that in the process of peptization a portion, although perhaps only a very small portion, of the solute goes into true solution. According to this hypothesis, acetone is regarded as a good solvent, not simply because of its high fluidity, but because it actually dissolves a greater portion of the nitrocellulose into true solution. (In the use of the term "true solution" we must avoid too hastily assuming that the colloid particles are completely broken up into simple unassociated molecules.)

When a substance dissolves in some solvent without dissociation or combination, the fluidity concentration curve is nearly linear.[5] When, however, the solute unites with the solvent, the fluidity concentration curve generally departs from the linear and the amount of the sagging of the curve may be used to calculate[6] the composition of the solvate as well as the amount of combination which has taken place. The mobility concentration curve of nitrocellulose is an extreme example of this type, indicating that the nitrocellulose molecule is highly solvated. But the mobility does not give us a measure of the solubility.

On the other hand, the yield value most certainly arises from the portion of the material which is not in true solution. As the solution is heated, the yield value grows smaller and finally disappears, at 43°C. in the case of acetone, and 71°C. for ether-alcohol extrapolated. At these temperatures we must assume that Newburgh nitrocellulose goes entirely into true solution. It has also been found that the rate of decrease of the yield value with the temperature is the same in both solvents, which seems to indicate that the temperature coefficient of solubility is the same in both solvents and at a given temperature the amount undissolved is measured by the yield value. Finally, it may be remarked that the temperature of zero yield value is not a melting point, although it may be regarded as analogous to the melting temperature. It may be generally true that the lower the temperature of zero yield value the greater the solubility, but since the solubility ratio may vary with the temperature, the yield values at a given temperature should alone be compared.

[5] BINGHAM, E. C.: *Lib. cit.*, pp. 160 *et seq.*

[6] *Idem.*, pp. 176 *et seq.*

Polar and Non-polar Colloids

Having thus briefly considered colloids of the emulsion type, it is well to take up colloids of the suspension type, since they differ from the former in important respects. Friedländer[7] supposed that small percentages of suspended substances do not affect the viscosity. This confusing result is a consequence of

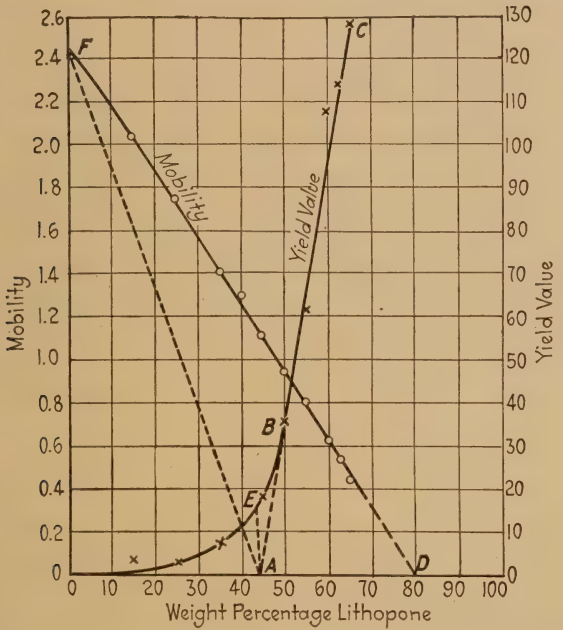


Fig. 5.—The variation in the yield value and mobility obtained by dilution of a suspension of lithopone in linseed oil with more linseed oil at 25°C.

the hyperbolic character of the viscosity-concentration curve. As soon as we plot fluidities or, still better, mobilities, we find that the curve is linear, as shown in Fig. 5 for lithopone suspended in linseed oil, so that very dilute suspensions do not present any anomaly whatever. This type of curve has been confirmed using substances of the most diverse type.

So far as is now known, the mobility-concentration curve for non-polar substances does not depart from linearity, even at high concentrations of the disperse phase. This is in marked

[7] *Z. physik. Chem.*, **24** (1897), 152.

contrast to the behavior of polar colloids, and this may serve as a distinguishing test between them. The mobility curve reaches a zero value at a finite concentration which seems to be intimately related to the pore space in the disperse phase, for, on purely theoretical grounds, we should expect to reach zero mobility with close packing without interlocking. According to this view the mobility-concentration curve is completely defined by the fluidity of the medium and the pore space of the disperse phase; and thus in the concentration of zero mobility we have another control point of some possible value. For spheres of equal size, cubical close packing would correspond to a concentration of 52.4 per cent by volume. We cannot suppose that lithopone is made up of spheres of equal size, nevertheless it is not without interest to observe that the concentration of zero mobility is 79.6 per cent by weight, which is 45.6 per cent by volume.

At the higher concentrations (above 43 per cent in lithopone and linseed oil, as shown in the figure) the yield value increases in a linear manner with the concentration. Assuming that this behavior is general for non-polar colloids, the concentration of zero yield value as found by extrapolation is significant as well as the manner in which the yield value increases with the concentration. The concentration of zero yield value is dependent upon the particle size of the disperse phase, but also to an extraordinary degree upon the adhesion between the medium and the disperse phase. Thus, a paint made up from a neutral mineral oil and lithopone was found to have its yield value lowered 80 per cent by the addition of only 0.2 per cent of oleic acid.

Since it has been customary to measure what we have here called "apparent fluidities" instead of mobilities, it may be remarked in passing that the apparent fluidities are always lower than the mobility and, with a very long capillary and a small pressure head, the apparent fluidity-concentration curve may approach the curve *FA* in Fig. 5 and may, therefore, be used to find the concentration of zero yield value.

As noted in the figure, there is evidence that the yield-value-concentration curve is not linear throughout its entire length. Very dilute suspensions show a very small though real yield value, as indicated by the part of the curve *BEO*. For greater

clarity of expression, the flow in suspensions having concentrations up to the point *A* may be referred to as pseudo-plastic. In explanation it may be said that the causes in operation in pseudo-plastic flow are probably different from those in true plastic flow. In the latter it is assumed that the particles touch each other, while in the former this is certainly not necessarily the case. In pseudo-plastic flow the energy is dissipated by the distortion of the stream lines of flow around the particles. In plastic flow this flowing of the medium ahead of the particles suspended is regarded rather as a correction term arising from *seepage*, but much more work is needed on this whole matter.

From what has preceded it would be inferred that all colloidal materials should show a yield value, but this conclusion is hardly justified. Gardner and Holdt[8] have shown that varnishes have a very small or even negligible yield value. Adding to a varnish several per cent of stearic acid or talc, as is done in making dental impression waxes, does not introduce a noticeable yield value, although it does greatly decrease the fluidity. Though at first surprising, this is quite in accordance with what was observed in the case of lithopone and linseed oil. The fluidity of these impression compounds is a linear function of the temperature over a range of 15 or more degrees, the fluidity reaching a zero value at a definite temperature. This temperature of zero fluidity is again a temperature of transition between viscous and plastic flow and it may serve as a useful control temperature in the case of very viscous liquids. A study of the plasticity constants below the transition temperature would also probably give useful information. As in the other transition temperatures which have been described in this chapter, this is certainly not a true melting point, because there is no sudden increase in fluidity at the transition point. Elsewhere the writer has attempted to give an explanation of this transition point.[9]

Perhaps even this brief treatment will suffice to suggest to the reader ways in which plasticity data can be utilized to advantage in colloid chemistry. The author must disclaim any attempt to give an exhaustive summary of those properties which might be studied with profit from the viewpoint of plastic-

[8] Paint Manufacturers' Assoc. of the U. S., Circular No. 127.

[9] *J. Phys. Chem.*, **28** (1924), 263.

ity. Hardness, malleability, ductility, and tensile strength tests all involve plastic flow. Important properties in the arts, scarcely recognized among standard physical properties, are length and shortness, which are applied to the most diverse materials, such as iron, dough, glue, paint, etc. These properties gain an entirely rational explanation on the basis of fluidity and plasticity relations. Apparently, quite distinct from the hardness which we recognize in metals is that "hardness" in certain fossil resins which makes them so highly valued in the manufacture of varnish. It can scarcely be doubted that this hardness is in some way connected with the resistance to flow exhibited in the varnish film and perhaps also in the original varnish resin.

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